(51) International Patent Classification 6 : C01D 15/02, C01G 45/02, H01M 4/50, 4/58	**A1**	(11) International Publication Number: **WO 00/23380** (43) International Publication Date: 27 April 2000 (27.04.00)

(54) Title: LITHIUM MANGANESE OXIDE AND METHODS OF MANUFACTURE

(57) Abstract

This invention relates to metal–doped lithium manganese oxide and methods of its production. In particular, it relates to stable lithium manganese oxide in monoclinic form, doped with one or more metal ion, the preferred dopants being one or both of aluminium and chromium. The method of the invention involves the synthesis of stable metal–doped lithium manganese oxide in monoclinic form by high temperature solid state reaction.

LITHIUM MANGANESE OXIDE AND METHODS OF MANUFACTURE

TECHNICAL FIELD

5   This invention relates to metal doped lithium manganese oxide and methods of its production.

BACKGROUND

10   Given the huge commercial success of rechargeable lithium batteries there is considerable interest in the development of improved intercalation compounds for use as the electrodes in such batteries. Appropriate compounds must possess a sufficient capacity for providing energy, must have appropriate electric conductivity and, preferably, should be stable at elevated temperatures. Furthermore, they must be able
15   to be produced in commercial quantities at a viable cost.

The trivalent manganese compound $LiMnO_2$ has been identified as a possible cathode material for lithium ion batteries. In particular, monoclinic (m-) $LiMnO_2$ (space group C2/m), having a layered rock salt structure similar to $LiCoO_2$ and
20      $LiNiO_2$, exhibits promising electrochemical properties. However, $LiMnO_2$ obtained via conventional solid state reaction usually has an orthorhombic (o-$LiMnO_2$) structure (space group Pmnm), since m-$LiMnO_2$ is not usually stable under these synthesis conditions.

25   To date, m-$LiMnO_2$ has been obtained by an ion exchange reaction of lithium salts with $NaMnO_2$ as precursor, or by a mixed alkaline-hydrothermal reaction (Armstrong & Bruce, Nature 381, 499 (1996); Tabuchi et. al., J. Electrochem. Soc, 145, L49 (1998)).

30   International patent application no. PCT/US97/18839, by Massachusetts Institute of Technology, discloses compositions having a general formula $Li_xM_yN_xO_2$,

2

and including the compound $LiAl_{0.25}Mn_{0.75}O_2$, being a layered monoclinic structure.
The added aluminium apparently stabilises the layered monoclinic modification and
allows direct synthesis of the compound. Chiang et al., in Electrochem. Solid State
Lett. $\underline{1}$, 13 (1998) describe the preparation of both $LiAl_{0.25}Mn_{0.75}O_2$ and

5   $LiAl_{0.05}Mn_{0.95}O_2$ in the layered monoclinic structure. However, the synthesis route
used to prepare the compounds in the above references (PCT/US97/18839 and Chiang
et al.) is based on the coprecipitation of the precursor hydroxides out of aqueous
nitrate solution and subsequent freeze drying of the obtained hydroxide mixture. The
dry mixture is then fired at 945°C in an inert atmosphere.

10

This synthesis method is complex and expensive and the nitrates of
aluminium and manganese may be carcinogens and mutagens. Thus, the method may
not be appropriate for commercial production.

15   Davidson et al. in United States patent No. 5,370,949 and J. Power Sources
$\underline{54}$, 205 (1995) disclose compounds of composition $Li_2Cr_xMn_{2-x}O_4$ prepared by high
temperature solid state reactions of lithium carbonate with chromium (III) oxide and
manganese (IV) oxide, or of $LiCrO_2$ with o-$LiMnO_2$. Compounds for which $x \geq 1.5$
apparently had a layered hexagonal structure similar to $LiCrO_2$. Compounds for which

20   $0.1 \leq x \leq 1.25$ gave X-ray diffraction patterns which could be indexed to a tetragonal
cell based on a structure like the lithiated spinel-related phase $Li_2Mn_2O_4$. Dahn et al.
in J. Electrochem. Soc. $\underline{145}$, 851 (1998) showed that the data described by Davidson
et al. in US 5,370,949 and J. Power Sources $\underline{54}$, 205 (1995) are better explained by a
monoclinic layered crystal structure.

25

The data published by Davidson et al. and Dahn et al., if taken in
combination, therefore demonstrate that chromium can be used in a solid state
reaction to stabilise a layered monoclinic structure for $LiCr_xMn_{1-x}O_2$ for $x \geq 0.05$
(dividing the subscripts in the formulae given by Davidson et al. and Dahn et al. by a

30   factor of 2 for consistency with other descriptions).

The selection of element or elements doped into $LiMnO_2$ and the proportions of dopant may be important in determining the extent to which a stable $LiMnO_2$ composition may be produced with the required electrochemical properties by a commercially viable process.

5

Moreover, a combination of dopants used to stabilise a layered monoclinic phase of $LiMnO_2$ may facilitate the synthesis procedure and/or provide electrochemical advantages over the prior art compounds using only aluminium or chromium as the dopant.

10

OBJECTS OF THE INVENTION

It is therefore an object of the present invention to provide a method of synthesising lithium manganese oxide intercalation compounds which reduces or
15   overcomes the abovementioned problems, or which at least provides the public with a useful alternative.

It is a further and/or alternative object of the present invention to provide lithium manganese oxide intercalation compounds having improved characteristics, or
20   at least to provide the public with useful alternative compounds.

Other objects of the present invention may become apparent from the following description which is given by way of example only.

4

SUMMARY OF THE INVENTION

According to one aspect of the present invention there is provided a
metal-doped lithium manganese oxide composition having the formula
5   $LiM^1_{m1}M^2_{m2}...M^x_{mx}Mn_zO_2$ wherein M^1, M^2...M^x are each different metal ions,
m1+m2+...mx+z is substantially equal to 1, m1+m2+...mx is greater than zero but less
than 0.75 and z and at least m_1 are each greater than zero, providing that where
m2...mx are zero M^1 is Cr and 0<m1<0.05 or M^1 is Ga.

10   Preferably, M^1, M^2...M^x are each selected to have an ionic radius in their
relevant oxidation state, similar to or less than that of Mn^{3+}.

Preferably, M^1, M^2...M^x are each selected from the group consisting of Al, Ga,
Cr, Co, Fe, B, V, Ti and Ru.

15
Preferably, M^1 may be Al.

Preferably, M^2 may be selected from Cr, Co, Fe, B, V, Ti and Ru and is most
preferably Cr.

20
Preferably, M^1, M^2...M^x each has the property of existing in a minimally
distorted octahedral sphere of co-ordination.

Preferably, M^1, M^2...M^x each has a formal oxidation state of 3^+.

25
Preferably, $m_1+m_2+...m_x$ may be greater than zero but less than about 0.25.

Preferably the composition is in predominantly monoclinic form.

30   According to a further aspect of the invention there is provided a method of
synthesising a metal-doped lithium manganese oxide composition having the formula
$LiM^1_{m1} M^2_{m2}...M^x_{mx} Mn_z O_2$ wherein M^1, M^2...M^x are each different metal ions,

m1+m2+...mx + z is substantially equal to 1, m1+m2+...mx is greater than zero but less than 0.75 and z and at least m1 are each greater than zero, providing that where m2...mx are zero and M^1 is Cr then 0<m1<0.05, in stable form by solid state reaction.

5   Preferably, the solid state reaction includes:

-        mixing reagents including a lithium compound, a manganese compound and at least one additional metal compound, each compound selected from an oxide, a hydroxide and/or a carbonate, and

10

-        heating the mixture in a reactor under inert atmosphere, to a temperature exceeding 800°C for more than 2 hours.

Preferably, the lithium compound may be lithium carbonate.

15

Preferably, the manganese compound may be manganese oxide.

Preferably, the or each metal of the at least one additional metal compound may be selected to have an ionic radius in its relevant oxidation state, similar to or less

20   than that of Mn^{3+}.

Preferably, the or each metal of the at least one additional metal compound may be selected from the group consisting of Al, Ga, Cr, Co, Fe, B, V, Ti and Ru.

25   Preferably, the at least one additional metal compound includes aluminium oxide. Preferably, a transitional alumina.

Preferably, the at least one additional metal compound alternatively, or in addition, includes chromium oxide.

30.

Preferably, the method may further include ball milling the mixed reagnts.

Preferably, the mixture may be heated to a temperature in the range substantially 900°C to 1080°C. More preferably substantially 1000°C to 1080°C for a period of at least 5 hours.

5   Preferably, the inert atmosphere may have a sufficiently low pO_2 to facilitate the formation of manganese in its 3+ oxidation state.

Preferably, the pO_2 may be substantially 10^{-5} atm or less.

10   Preferably, the mixture may be heated in a reactor having a high temperature stable lining.

According to a further aspect of the invention there is provided a method of synthesising a metal-doped lithium manganese oxide composition of the formula
15     $LiM^1_{m1}M^2_{m2}...M^x_{mx}Mn_2O_2$ wherein M^1, M^2...M^x are each different metal ions, m1+m2+...mx+z is substantially equal to 1, m1+m2+...mx is greater than zero but less than 0.75 and z and at least m1 are each greater than zero, in stable predominantly monoclinic form, the method including the steps of:

20   -   mixing reagents including a lithium compound, a manganese compound and at least one additional metal compound, each compound selected from an oxide, a hydroxide and/or a carbonate,

        -   heating the mixture in air to a temperature ≥ 200°C for at least 5 hours to
25   produce oxygen-rich lithium manganese oxides,

        -   further heating the mixture in a reactor under inert atmosphere to a temperature exceeding 800°C for at least 2 hours.

30

7

Preferably the heating in air may be at a temperature in the range 600 to 850°C. Most preferably substantially 700°C.

Preferably the heating under inert atmosphere may be at a temperature of 5   substantially 1000 to 1080°C.

According to a further aspect of the present invention there is provided a method of synthesising a metal doped lithium manganese oxide composition substantially as herein described and with reference to the accompanying examples.

10
Other aspects of the present invention may become apparent from the following description which is given by way of example only and with reference to the accompanying examples.

15   **BRIEF DESCRIPTION OF FIGURES**

Figure 1:   Effect of temperature on $LiMnO_2$ production by high temperature solid state reaction with metal doping in a steel reactor in accordance with Example I.

20

Figure 2:   Effect of reaction time on $LiMnO_2$ production in accordance with Example I.

Figures 3 A-F: X-ray diffraction patterns showing the effects of
25   temperature on the production and phase of $LiMnO_2$ from a high temperature solid state reaction with metal doping in an alumina-lined reactor in accordance with Example II:

                              • - $o\text{-}LiMnO_2$
30   + - $m\text{-}LiMnO_2$
                              o - Li_2MnO_3

$* - Mn_3O_4$

Figures 4 A-D:	X-ray diffraction patterns showing the effects of chromium doping on the production and phase of $LiMnO_2$ from a high temperature solid state reaction with metal doping in an alumina-lined reactor, in accordance with Example IV:

   • - $o-LiMnO_2$

   + - $m-LiMnO_2$

   o - $o-Li_2MnO_3$

   * - Mn_3O_4

   ♦ - $LiCrO_2$

Figure 5:	X-ray diffraction patterns of $LiCr_xMn_{1-x}O_2$ for x= 0.01, 0.03, 0.05, 0.10 and 0.20, prepared according to Example V (+ = $m-LiMnO_2$, o = $o-LiMnO_2$).

Figure 6:	X-ray diffraction pattern of $LiAl_{0.05}Mn_{0.95}O_2$ prepared according to Example VI (+ = $m-LiMnO_2$, o = $o-LiMnO_2$).

Figure 7:	Schematic representation of the cell construction as used in Examples VI, VII, VIII and X.

Figure 8:	X-ray diffraction pattern of $LiAl_{0.10}Mn_{0.90}O_2$ prepared according to Example VII (o = $o-LiMnO_2$, all other peaks $m-LiMnO_2$).

Figures 9A-D:	X-ray diffraction patterns of (A) $LiAl_{0.05}Cr_{0.01}Mn_{0.94}O_2$, (B) $LiAl_{0.05}Cr_{0.03}Mn_{0.92}O_2$, (C) $LiAl_{0.05}Cr_{0.05}Mn_{0.90}O_2$,

9

and (D) $LiAl_{0.02}Cr_{0.05}Mn_{0.93}O_2$ prepared according to
Example VIII (o = o-LiMnO$_2$).

Figures 10A&B: X-ray diffraction patterns of (A) $Li_{0.5}Cr_{0.05}Mn_{0.95}O_2$ and

5

(B) $LiCr_{0.05}Mn_{0.95}O_2$ prepared according to Example
IX.

Figures 11A&B: X-ray diffraction patterns of $LiAl_{0.05}Mn_{0.95}O_2$ prepared
according to Example X (A) after air step (* = spinel,

10

= Li_2MnO_3), (B) after nitrogen step (o = o-LiMnO$_2$).

Figures 12A&B: X-ray diffraction patterns of (A) $Li_{0.5}Ga_{0.10}Mn_{0.90}O_2$ and
(B) $LiGa_{0.10}Mn_{0.90}O_2$ prepared according to Example XI
(o = o-LiMnO$_2$).

15

Figures 13A-D: X-ray diffraction patterns of (A)
$Li_{0.5}Cr_{0.05}Ga_{0.05}Mn_{0.90}O_2$, (B) $LiCr_{0.05}Ga_{0.05}Mn_{0.90}O_2$, (C)
$Li_{0.5}Cr_{0.05}B_{0.05}Mn_{0.90}O_2$, and (D) $LiCr_{0.05}B_{0.05}Mn_{0.90}O_2$
prepared according to Example XII (o = o-LiMnO$_2$).

20

DETAILED DESCRIPTION OF THE INVENTION

Investigations were carried out to identify new metal-doped $LiMnO_2$

25   compositions and provide a robust, simple and commercially viable solid state
synthesis of aluminium, chromium and/or other metal doped layered monoclinic m-
$LiMnO_2$, which could have commercial significance as a cathode in lithium ion
batteries.

30   The basic reaction underlying the synthesis method and compositions of the
present invention involves the conversion of, for example, lithium carbonate and

10

manganese oxide to lithium manganese oxide. One possible reaction scheme would
be:

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

$$2 MnO_2 \rightarrow Mn_2O_3 + \tfrac{1}{2}O_2$$

5        $$Li_2O + Mn_2O_3 \rightarrow 2LiMnO_2.$$
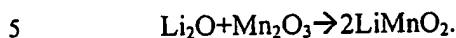
The invention involves methods of synthesising stable forms of metal-doped
$LiMnO_2$, in layered monoclinic form, by solid state reaction. The invention also
relates to specific stable compositions formed by these methods.

10

Preferred, stable compositions were produced with the starting reagents
lithium carbonate (Li_2CO_3), manganese (IV) oxide (MnO_2) and aluminium oxide
(Al_2O_3) heated in a reactor under inert atmosphere to a temperature in the range 800°C
to 1080°C for a period of at least 2 hours. The formation of $LiMnO_2$ in monoclinic form,

15   may be facilitated by raising the temperature to between about 950°C and 1080°C, and
using a transitional alumina as the source of aluminium.

Other preferred, stable compositions were produced with the starting reagents
lithium carbonate (Li_2CO_3), manganese (IV) oxide (MnO_2), aluminium oxide (Al_2O_3)

20   and chromium oxide (Cr_2O_3) heated in a reactor under inert atmosphere to a
temperature in the range 800°C to 1080°C for a period of at least 2 hours.

Other preferred, stable compositions were produced in a two-stage reaction by
firstly reacting lithium carbonate (Li_2CO_3) and manganese carbonate ($MnCO_3$) with

25   one or more of aluminium oxide (Al_2O_3), chromium oxide (Cr_2O_3), gallium oxide
(Ga_2O_3) and boric acid (H_3BO_3) in air at a temperature of 600-850 °C to produce
oxygen-rich lithium manganese oxides, followed by a second heating step under
nitrogen at 800-1080 °C.

30   In this two-stage reaction, if the lithium, manganese and dopant reagents in
the first stage are combined in the appropriate ratios to give a product with a

lithium/(manganese + dopant) molar ratio of 1, the reaction in air will produce a two phase mixture of a spinel phase $Li_xMn_{2-x}O_4$ and rock salt phase Li_2MnO_3. Both phases may contain the dopant elements in their crystalline structure. When this product is heated under N_2 flow, the two phases react together to give doped $LiMnO_2$ according to the reaction scheme:

$$LiM_{2x}Mn_{2-2x}O_4 + Li_2M_xMn_{1-x}O_3 \rightarrow 3\ LiM_xMn_{1-x}O_2 + \frac{1}{2}O_2$$
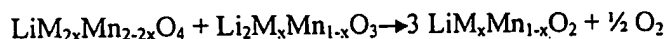
where M may be one or more dopant elements.

Alternatively, the reagents in the first stage can be combined in the appropriate ratios to give a product with a lithium/(manganese + dopant) ratio of approximately 0.5. The product of the reaction in air will then be a single-phase doped spinel oxide. This can then be combined with additional Li reactant in the second stage under N_2 to give doped $LiMnO_2$, e.g.:

$$LiM_{2x}Mn_{2-2x}O_4 + \frac{1}{2}Li_2CO_3 \rightarrow 2\ LiM_xMn_{1-x}O_2 + \frac{1}{2}CO_2 + \frac{1}{2}O_2$$
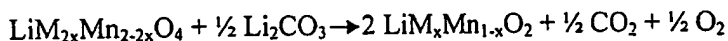
An advantage of the two-stage method is that the dopant precursor compounds are reacted with the manganese precursor compound in air, which provides more reactive conditions for the decomposition of some metal salts than an inert atmosphere such as N_2. This may allow the selection of metal salts as starting compounds which may be difficult to react together to give a single-phase product under an inert atmosphere. Spinel $LiMn_2O_4$ can be prepared with a large number of different dopants at a range of concentrations. Many of these doped $LiMn_2O_4$ compounds are known and have been well characterised in terms of the effects of the dopant element on the crystal structure. This allows for ready identification of the doped spinel intermediate phase by techniques such as X-ray powder diffraction. The relatively facile formation of doped spinel phases in air then provides an atomic-level dispersion of the dopant element in the manganese oxide lattice before proceeding to the conversion step under N_2. The conversion step under N_2 therefore involves

12

essentially lithium diffusion into the spinel phase from the Li_2MnO_3 phase or additional Li reactant, some reduction of Mn^{4+} to Mn^{3+}, and an accompanying crystal phase transformation.

5   It will be appreciated by those skilled in the art that different lithium, manganese and dopant compounds may also be employed as the starting reagents, but generally selected from carbonates, oxides and hydroxides.

It is considered that the metal ions most preferred for doping of the $LiMnO_2$
10   should be selected by several criteria, firstly ionic radius, and secondly appropriate charge state. The incorporation of a metal ion with an ionic radius similar to or less than that of Mn^{3+} is likely to mitigate the distortion of the octahedral geometry around the Mn^{3+}. Thus, preferably, the metal ion or ions should have an ionic radius, in their relevant oxidation state, similar to or less than that of Mn^{3+}. Hence, as an alternative
15   to, or in addition to aluminium, the dopants may be selected from, for example, B, Ga, Cr, Co, Fe, V, Ti and Ru. Preferably, the metal ion or ions may also have the property of existing in a minimally distorted octahedral sphere of co-ordination.

20   **Example I**
Exact stoichiometric amounts (based on $LiAl_{0.05}Mn_{0.95}O_2$) of lithium carbonate (99.9% pure), manganese (IV) oxide (90+% pure) and aluminium oxide (99.8% pure) were weighed out, mixed and subsequently homogenised for 30 minutes using a vibrating table. These mixtures were finally fired
25   under inert atmosphere (BOC, Zero Grade Nitrogen <5ppm O_2, flow rate = 5Lmin^{-1}) in a proprietary stainless steel rotary reactor fitted inside a muffle furnace. After reaction the reactor was removed from the muffle furnace and cooled to <50°C by blowing air across the reactor body whilst maintaining the inert atmosphere. The duration of the described cooling process was
30   approximately 20 minutes.

13

To evaluate the temperature effect precursor mixtures were fired at temperatures between 700°C and 1120°C. The reaction time was usually between 3 and 5 hours. The produced samples were analysed using X-Ray diffraction (XRD) to assess phase purity. The monoclinic polymorph of

5   LiMnO$_2$ started to form at 1000°C. The other phases identified by XRD were orthorhombic o-LiMnO$_2$, tetragonal LiAlO$_2$, and rock salt Li$_2$MnO$_3$. The latter, and the spinel phase LiMn$_2$O$_4$, were preferentially formed if the oxygen partial pressure in the reactor exceeded 10^{-4}atm. Thus, the inert atmosphere should preferably involve a pO$_2$ of 10^{-5} atm or less. This is sufficient to

10   facilitate the formation of manganese in its 3+ oxidation state.

The effect of temperature is summarised in Figure 1.

The highest amounts of the monoclinic polymorph m-LiMnO$_2$ were obtained

15   at 1060°C, yielding 85% m-LiMnO$_2$, 5% o-LiMnO$_2$, 5% of LiAlO$_2$, and 5% Li$_2$MnO$_3$.

It should be noted that this reaction was performed with in-situ grinding by means of a steel rod.

20

Higher temperature (above 1060°C) appeared to reduce the amount of the monoclinic phase.

More detailed temperature effect results, and X-ray diffraction data are

25   included below under Example II.

Samples of the end product were digested in hydrochloric acid and hydrogen peroxide and subsequently analysed by AA (for Li) and ICP-OES (for Mn and Al). The molar ratio Li:Al:Mn was found to be substantially 1.00:0.05:0.95$\pm$

30   5%.

14

Reaction time was investigated at a constant reaction temperature of 1060°C.
The results are shown in Figure 2.

5   The reaction seems to be completed in approximately three hours. Reaction
times of longer than 5 hours usually lead to a decrease of the $LiMnO_2$-phases
and the formation of spinel phase. Reaction time and temperature are likely
to be dependent on particle size, and the required reaction may be achieved in
a shorter time employing reagents, particularly manganese oxide, having a
smaller particle size.

10

Example II

In the following example an alumina-lined steel reactor was employed in
place of a conventional rotary stainless steel reactor.

15   Exact stoichiometric amounts (based on $LiAl_{0.05}Mn_{0.95}O_2$) of lithium
carbonate (99.9% pure), manganese (IV) oxide (90% + to <99.0% pure) and
aluminium oxide (99.8% pure) were homogenised for 30 minutes using a
vibrating table. The resulting mixtures were fired at temperatures between
800°C and 1100°C under inert atmosphere (BOC, zero grade nitrogen) in
20   alumina-lined stainless steel rotary reactors fitted inside a muffle furnace and
cooled to less than 50°C by blowing air across the reactor body whilst
maintaining the inert atmosphere.

Samples resulting from processing for about 5 hours at 1040°C had average
25   phase compositions of approximately 80% o-$LiMnO_2$ and 10% m-$LiMnO_2$.

X-ray diffraction patterns (see Figure 3 A-F) showed a clear shift in the
proportion of $LiMnO_2$ at a temperature of 950°C (compare Figures 3C and D)
and higher, and clear identification of the monoclinic form at a temperature of
30   1050°C (Figure 3F). However, as can be seen from Table 1, the proportion of

phases was unexpected in comparison with the results of Example I using a stainless steel reactor. Even at 1050°C there was only about 15% m-LiMnO₂.

Table 1: Temperature effect on LiMnO₂ proportions and phases, all at 5 hours reaction time

Temperature °C	Li_2MnO_3 %	$o\text{-}LiMnO_2$ %	$m\text{-}LiMnO_2$ %	Mn_3O_4 %
800	35	50	0	15
850	25	65	0	10
900	30	60	0	10
950	5	90	0	5
1000	<5	~95	0	<5
1050	≤5	80	15	0

Elemental analysis revealed the presence of high amounts of iron and chromium in samples produced in the conventional steel reactors in comparison with the samples produced in alumina-lined reactors. The Fe content of samples prepared in a steel reactor was generally in the range 1-3%, with Cr in the range 0.05-0.2%. These figures were reduced by about a factor of 10 in the alumina reactor.

It was concluded that a few percent of one or both of Fe and Cr, transferred into the reaction mixture from the steel reactor, aided the formation of the monoclinic LiMnO₂ phase under reaction conditions where it is otherwise difficult to form m-LiMnO₂.

Example III
The process of Example II was repeated in alumina boats in a tube furnace, with the addition of chromium (in the form of Cr_2O_3) to the reaction mixture and subsequent firing at temperatures from 1050 to 1100°C for 3 to 7 hours, under an inert atmosphere. As in Example II, the mixture was first heated to

16

about 200°C for about an hour before increasing the temperature to the selected level. The results are shown in Table 2.

Table 2: Chromium doping of Aluminium-doped LiMnO$_2$

5

Cr$_2$O$_3$ Content wt%	Reaction Temp/time °C/h	o-LiMnO$_2$ %	m-LiMnO$_2$ %	Υ-LiAO2 %	LiCrO$_2$ %	Li$_2$MnO$_3$ %
1	1050/5	5	80	5	0	10
2	1050/5.5	0	95	0	0	5
2.5	1050/7	0	80	5	5	10

10 As can be seen from Table 2, the presence of Cr$_2$O$_3$ 1 to 2.5 wt%, with a reaction temperature of 1050°C for a period of at least 5 hours, resulted in a marked change in the phase composition of the end product in comparison with the results obtained under similar conditions, but without chromium, in the alumina-lined reactor.

15 Whilst these results were obtained using chromium oxide, it is anticipated that other metals (such as Co and Fe) or combinations of metals would similarly facilitate the formation of Al-doped m-LiMnO$_2$. It is also considered that the chromium, or an alternative metal, may reduce the temperature at which Al-doped m-LiMnO$_2$ is formed.

20

17

Example IV

The effects of chromium doping were investigated in an alumina-lined reactor using the reagents described for Example II with the addition of chromium oxide (Cr_2O_3), and at 1050°C for 5 hours.

X-ray diffraction patterns for compositions resulting from the use of different starting proportions of Cr_2O_3 are shown in Figures 4A - D. X-ray diffraction analysis revealed the estimates shown in Table 3 for the content of the compositions.

Table 3: Chromium doping of aluminium-doped $LiMnO_2$, in alumina reactor

Cr_2O_3 Content wt%	Reaction Temp/time °C/h	o-$LiMnO_2$ %	m-$LiMnO_2$ %	Υ-$LiAlO2$ %	$LiCrO_2$ %	Li_2MnO_3 %
2	1050/5	40	50	0	0	10
3	1050/5	45	35	5	5	5
5	1050/5	15	70	0	10	5
7	1050/5	20	65	0	10	5

At 3 wt% Cr_2O_3, $LiMnO_2$ was still predominantly in the orthorhombic form (45%), although there was a 35% proportion of monoclinic form contrasting with only 15% under the same conditions but without chromium doping (see Figure 3). With 5 wt% Cr_2O_3, $LiMnO_2$ was predominantly in the monoclinic form (70%). The higher proportion of chromium oxide required in this Example compared with Example III could indicate inadequate mixing of the starting materials. Pregrinding of the reaction mixture could significantly improve the effect of chromium.

Example V

The effects of doping chromium alone in small quantities in $LiMnO_2$ were systematically investigated in a vertical cylindrical reactor lined with a high

18

temperature stable lining. Exact stoichiometric amounts of lithium carbonate (99.9% pure), MnO_2 (99.0% pure) and Cr_2O_3 (99.0% pure) to give products of formula $LiCr_xMn_{1-x}O_2$, where x= 0.01, 0.03, 0.05, 0.10, and 0.20, were mixed and ball-milled for 24 hours in a rotating shaker. The resulting mixtures were

5   loaded into the bottom of the reactor and fired at 1000 °C for 5 hours with a flow of zero grade nitrogen percolating through the reaction mixture from an inlet at the bottom of the reactor, with stirring at regular intervals to ensure homogeneity. Elemental analyses of the products using the method described in Example VI confirmed that the end products had the correct Li:Cr:Mn

10   ratios.

The X-ray diffraction patterns of the products are shown in Figure 5. The phase mixtures obtained, estimated from the X-ray diffraction analyses of the products, are given in Table 4. When x is between 0.05 and 0.20 the products

15   are 100% single phase monoclinic $LiCr_xMn_{1-x}O_2$, as indicated by the data of Davidson et al. in J. Power Sources 54, 205 (1995) and Dahn et al. in J. Electrochem. Soc. 145, 851 (1998). However the results show that predominantly monoclinic $LiCr_xMn_{1-x}O_2$ can also be obtained when x=0.01 or 0.03, a result not predicted by the aforementioned publications.

20

Table 4: Chromium doping of $LiMnO_2$ at 1000 °C

x in $LiCr_xMn_{1-x}O_2$	% orthorhombic phase	% monoclinic phase
0.01	30	70
0.03	10	90
0.05	0	100
0.10	0	100
0.20	0	100

25   The monoclinic layered structure (space group C2/m) of the $LiCr_xMn_{1-x}O_2$ products was confirmed by Rietveld analysis of the X-ray diffraction data. The unit cell parameters calculated from the X-ray diffraction data by the Rietveld refinement method are shown in Table 5 for the single-phase monoclinic $LiCr_xMn_{1-x}O_2$ products where x=0.05, 0.10 and 0.20, compared

with published data for non-doped monoclinic layered $LiMnO_2$ (Capitaine et al., Solid State Ionics 89, 197 (1996)).

Chromium doping results in changes in the crystal unit cell dimensions consistent with substitution of Cr ions into Mn sites of the crystal structure. In $LiMnO_2$, the extent of the monoclinic crystal distortion resulting from the Jahn Teller distortion of the octahedral coordination environment around the Mn ions is reflected in the magnitude of the ratio between the a and b crystal axes. The systematic decrease in the a/b ratio with increasing amounts of Cr in the crystal is an effect of a minimally distorted octahedral sphere of co-ordination around the Cr ions. The atomic positions of the cations in the crystal lattice were also refined using the Rietveld method. The results confirmed that Cr and Mn ions share the transition metal sites in the layered crystal structure. No Mn or Cr ions were detected in the interlayer (lithium) sites of the crystal.

Table 5: Unit cell parameters for the single-phase monoclinic $LiCr_xMn_{1-x}O_2$ products

x in $LiCr_xMn_{1-x}O_2$	$a(Å)$	$b(Å)$	$c(Å)$	$\beta(°)$
0.00*	5.439(3)	2.809(2)	5.395(4)	115.9(4)
0.05	5.434(1)	2.809(1)	5.389(2)	115.98(2)
0.10	5.405(2)	2.815(1)	5.375(2)	115.61(2)
0.20	5.382(3)	2.823(1)	5.350(3)	115.05(4)

* Capitaine et al. (Solid State Ionics 89, 197 (1996)).

Example VI

The effects of using a transitional alumina as the source of Al in the solid state reaction were investigated in a vertical cylindrical reactor with a high

temperature stable lining. Exact stoichiometric amounts of lithium carbonate (99.9% pure), MnO_2 (99.0% pure) and theta-Al_2O_3 (99.95% pure) to give a product of formula $LiAl_{0.05}Mn_{0.95}O_2$ were mixed and ball-milled for 30 minutes. The resulting mixture was loaded into the bottom of the reactor and

5   heated to 1000°C for 3.5 hours with a flow of zero grade nitrogen percolating through the reaction mixture from an inlet at the bottom of the reactor, with stirring at regular intervals to ensure homogeneity. After 3.5 hours the product was allowed to cool in the furnace over a period of 15 hours, maintaining the nitrogen flow until the temperature dropped below 50 °C.

10

The X-ray diffraction pattern of the product, shown in Figure 6, shows that the product contains approximately 90% m-$LiMnO_2$, and approximately 10% o-$LiMnO_2$. No additional impurity phases were detected.

15   Samples of the product were digested in hydrochloric acid and hydrogen peroxide and analysed by AA (for Li) and ICP-OES (for other metal ions). The molar ratio Li:Al:Mn was found to be 1.03:0.05:0.94, consistent with the expected stoichiometry within experimental error (±5%) of the analytical technique. Less than 0.1% Cr, 0.1% Ni, and 0.4% Fe were detected in the

20   product, indicating that contamination from the reactor lining was negligible and unlikely to have contributed to the formation of the monoclinic phase.

The formation of a predominantly monoclinic structure at 1000 °C in this case is attributed mainly to the higher reactivity of the theta-Al_2O_3 by comparison

25   with the aluminium-containing reactants used in the preceding examples. When the reaction was carried out under the same conditions but using an alpha-Al_2O_3 as the source of aluminium, mainly orthorhombic $LiMnO_2$ was produced. When alpha-Al_2O_3 was used, XRD also detected traces of $LiAlO_2$ in the product. This was not observed when the theta-Al_2O_3 was used,

30   suggesting that a more complete reaction of the Al_2O_3 with the manganese

oxide is the critical factor favouring the formation of monoclinic phase under these particular conditions.

The unit cell parameters for the monoclinic phase, obtained by performing a simultaneous Rietveld refinement of the crystal parameters for both the monoclinic and the orthorhombic phase from the X-ray diffraction data, are compared with those given by Capitaine et al. (Solid State Ionics $\underline{89}$, 197 (1996)) for non-doped monoclinic $LiMnO_2$ in Table 6. The monoclinic $LiAl_{0.05}Mn_{0.95}O_2$ phase of this example shows a contracted crystal lattice by comparison with the undoped compound. This is consistent with the presence of the Al ion, which has a smaller ionic radius than trivalent Mn, sharing the same crystallographic site as Mn. The contraction is more significant along the a crystal axis than the b crystal axis, consistent with a minimally distorted octahedral sphere of co-ordination around the Al ions since the magnitude of the a/b ratio is related to the average degree of distortion of the octahedron of oxygen ions around the cations in the Mn layer.

Table 6: Unit cell parameters for the monoclinic $LiAl_{0.05}Mn_{0.95}O_2$ phase of Example VI, compared with reported values for undoped monoclinic $LiMnO_2$ (Capitaine et al.)

	$a(A)$	$b(A)$	$c(A)$	$\beta(°)$
$LiAl_{0.05}Mn_{0.95}O_2$	5.419(2)	2.802(1)	5.381(2)	115.89(2)
$LiMnO_2$ (Capitaine et al.)	5.439(3)	2.809(2)	5.395(4)	115.9(4)

These results demonstrate that the choice of alumina reagent and ball milling of the reactant mixture before heating can influence the temperature at which a predominantly monoclinic form of aluminium doped $LiMnO_2$ is obtained using the solid state reaction method of the invention.

Electrodes were prepared by mixing 80 wt.% of $LiAl_{0.05}Mn_{0.95}O_2$, 12 wt.% acetylene black and 8 wt.% poly(vinylidene fluoride) as a slurry in 1-methyl-2-pyrrolidinone (NMP). The slurry was coated onto aluminium foil. After evaporation of the solvent, the coating was pressed on the aluminium foil and

annealed at 150 °C under vacuum. Circular electrodes measuring 14 mm in diameter were then punched from the coated foil. The circular electrodes were weighed individually and the active mass (the total weight of the circular electrode multiplied by the fraction of the electrode weight made up by

5   $LiAl_{0.05}Mn_{0.95}O_2$) calculated. The electrodes were then dried at 150 °C under vacuum to remove traces of water and transferred to an argon-filled dry glove box (<1 ppm water).

The electrodes were assembled into electrochemical cells within the argon-

10   filled glove box using 2032 button cell hardware. The cell assembly is schematically illustrated in Figure 7. The electrode containing the $LiAl_{0.05}Mn_{0.95}O_2$ was the cathode 1. The anode 2 was a circular disk of lithium foil having a thickness of 0.38 mm, pressed into a stainless steel lid 3. A polymeric gasket 4 was then positioned over the lip of the lid. A porous

15   glass fibre disk separator 5 wetted with 1M $LiPF_6$ in (50 wt.% ethylene carbonate + 50 wt.% dimethylene carbonate) electrolyte solution was placed between the anode and cathode. A stainless steel disk 6 and spring 7 were then positioned behind the cathode and the entire assembly hermetically closed within the stainless steel casing 8 by crimp sealing.

20

Cells prepared by this procedure were cycled more than 200 times between 2.0 and 4.4 V at ambient temperature and elevated temperature (55 °C). A constant charging current of 30 or 75 mA/g was applied until 4.4 V was reached, then the cell was held at 4.4 V until the current dropped below 3

25   mA/g. Cells were discharged at constant currents of 30 or 75 mA/g. Typical discharge capacities obtained by this procedure at the 30 mA/g discharge rate are given for the 1st, 16th, and 200th cycles in Table 8 in Example VIII. The discharge capacities at ambient temperature increase with cycling. At 55 °C the discharge capacities are particularly high and show good stability.

30

Example VII

Exact stoichiometric amounts of lithium carbonate (99.9% pure), MnO_2 (99.0% pure) and theta-Al_2O_3 (99.95% pure) to give a product of formula $LiAl_{0.10}Mn_{0.90}O_2$ were mixed and ball-milled for 30 minutes. The resulting mixture was loaded into the bottom of the reactor described in Example VI and heated to 1050°C for 10 hours under a flow of zero grade nitrogen. After 10 hours the product was allowed to cool in the furnace over a period of 15 hours, maintaining the nitrogen flow until the temperature dropped below 50°C.

The X-ray diffraction pattern of the product, shown in Figure 8, shows that the product contains approximately 95% m-$LiMnO_2$, with the remainder being o-$LiMnO_2$ phase. No additional impurity phases were detected.

The unit cell parameters of the monoclinic phase, calculated from the XRD pattern, are $a = 5.416(2)$ Å, $b = 2.804(1)$ Å, $c = 5.382(2)$ Å, and $\beta = 115.91°$. Like the monoclinic $LiAl_{0.05}Mn_{0.95}O_2$ phase of Example VI, the $LiAl_{0.10}Mn_{0.90}O_2$ material of this example shows a contracted crystal lattice by comparison with the undoped compound.

Electrodes and electrochemical cells containing the $LiAl_{0.10}Mn_{0.90}O_2$ material were prepared as described in Example VI, and the cells were charged and discharged following the same procedures. Typical discharge capacities obtained at the 30 mA/g discharge rate are given for the 1st, 16th, and 200th cycles at ambient and 55 °C in Table 8 in Example VIII. The material shows slightly lower initial capacities than the $LiAl_{0.05}Mn_{0.95}O_2$ compound of Example VI, but the capacity increases with cycling to values which are similar to those of the $LiAl_{0.05}Mn_{0.95}O_2$ material.

24

Example VIII

Compositions $LiAl_xCr_yMn_{1-x-y}O_2$ were prepared by reacting lithium carbonate (99.9% pure), MnO_2 (99.0% pure), theta-Al_2O_3 (99.95% pure) and Cr_2O_3 (99.0% pure). Exact stoichiometric amounts of the reactants to give the compositions $LiAl_{0.05}Cr_{0.01}Mn_{0.94}O_2$, $LiAl_{0.05}Cr_{0.03}Mn_{0.92}O_2$, $LiAl_{0.05}Cr_{0.05}Mn_{0.90}O_2$; and $LiAl_{0.02}Cr_{0.05}Mn_{0.93}O_2$ were mixed and ball-milled for 24 hours in a rotating shaker, then loaded into the vertical cylindrical reactor of Example VI and heated at 1050 °C for 5 hours under a flow of zero grade nitrogen.

The X-ray diffraction patterns of the products are shown in Figure 9(A-D). In the case of the compositions $LiAl_{0.05}Cr_{0.01}Mn_{0.94}O_2$ and $LiAl_{0.05}Cr_{0.03}Mn_{0.92}O_2$, the products were 80-90 % layered monoclinic phase, with the remaining phase being o-$LiMnO_2$. No other impurity phases were observed. The compositions $LiAl_{0.05}Cr_{0.05}Mn_{0.90}O_2$ and $LiAl_{0.02}Cr_{0.05}Mn_{0.93}O_2$ were phase-pure layered monoclinic materials. Cell parameters for these phases are given in Table 7.

Table 7: Unit cell parameters for the monoclinic $LiAl_xCr_yMn_{1-x-y}O_2$ products

x and y in $LiAl_xCr_yMn_{1-x-y}O_2$	a (Å)	b (Å)	C (Å)	β (°)
$x = 0.05, y = 0.01$	5.424	2.805	5.394	115.87
$x = 0.05, y = 0.03$	5.426	2.809	5.390	115.90
$x = 0.05, y = 0.05$	5.408	2.808	5.375	115.77
$x = 0.03, y = 0.05$	5.415	2.810	5.379	115.78

Electrodes and electrochemical cells containing the $LiAl_{0.05}Cr_{0.05}Mn_{0.90}O_2$, and

$LiAl_{0.02}Cr_{0.05}Mn_{0.93}O_2$ materials were prepared as described in Example VI,

and the cells were charged and discharged following the same procedures.

Typical discharge capacities obtained at the 30 mA/g discharge rate are given

5   for the 1st, 16th, and 200th cycles at ambient temperature and 55 °C in Table 8.

The cells cycled at 55 °C showed similar excellent capacity retention over 200

cycles as the $LiAl_{0.05}Mn_{0.95}O_2$ and $LiAl_{0.10}Mn_{0.90}O_2$ materials of Examples VI

and VII. However the $LiAl_{0.05}Cr_{0.05}Mn_{0.90}O_2$, and $LiAl_{0.02}Cr_{0.05}Mn_{0.93}O_2$

materials showed increased overall capacity at both 55 °C and ambient

10   temperature when compared with the $LiAl_{0.05}Mn_{0.95}O_2$ and $LiAl_{0.10}Mn_{0.90}O_2$.

materials.

The combination of chromium plus aluminium together in monoclinic layered

$LiMnO_2$ therefore provides a material with improved cycling characteristics

15   over monoclinic layered $LiMnO_2$ doped with aluminium alone. The addition

of chromium to the aluminium-doped $LiMnO_2$ also facilitated the obtaining of

a single-phase monoclinic layered material.

20   **Table 8:** Discharge capacities for the monoclinic $LiAl_xMn_{1-x}O_2$
materials of Examples VI, VII & IX, and the $LiAl_xCr_yMn_{1-x-y}O_2$ materials
of Example VIII.

Material	Example	Discharge capacity (mAh/g) at 30 mA/g current rate 4.4-2 V					
		Ambient temperature			55 °C		
		Cycle 1	Cycle 16	Cycle 196	Cycle 1	Cycle 16	Cycle 196
$LiAl_{0.05}Mn_{0.95}O_2$	VI	82	82	139	156	164	168
$LiAl_{0.05}Mn_{0.95}O_2$	X	92	92	140	161	177	152
$LiAl_{0.10}Mn_{0.90}O_2$	VII	73	73	143	137	162	168
$LiAl_{0.05}Cr_{0.05}Mn_{0.90}O_2$	VIII	93	80	127	158	182	184
$LiAl_{0.02}Cr_{0.05}Mn_{0.93}O_2$	VIII	122	138	122	170	184	170

26

Example IX

Exact stoichiometric amounts of lithium carbonate (99.9% pure), manganese carbonate (99.5% pure) and Cr_2O_3 (99.0% pure) to give a product of formula $Li_{0.5}Cr_{0.05}Mn_{0.95}O_2$ were mixed and ground in an acetone slurry using a mortar

5   and pestle. The mixture was loaded into a vessel formed from an inert metal alloy and fired in a furnace at 700 °C for 20 hours in air. The X-ray diffraction pattern of the product, in Figure 10A, shows that it was a single phase cubic spinel with a unit cell parameter of $a = 8.235$ Å. The X-ray diffraction data are consistent with doping of the chromium on the manganese site of spinel

10     $LiMn_2O_4$.

This compound was ground in acetone with an equivalent of lithium carbonate to give a product of formula $LiCr_{0.05}Mn_{0.95}O_2$, and heated under a flow of zero grade nitrogen at 1000 °C for 18 hours. The X-ray diffraction

15   pattern of this product, in Figure 10B, shows formation of phase-pure monoclinic layered $LiMnO_2$, with unit cell parameters $a = 5.431$ Å, $b = 2.807$Å, $c = 5.382$ Å, and $\beta = 115.94$ °. These cell parameters are very close to those obtained for the $LiCr_{0.05}Mn_{0.95}O_2$ compound of Example V.

20   This example shows that a two stage solid state process, in which a doped spinel phase is formed by reaction in air and then reacted with additional lithium under nitrogen, can be used to synthesise doped $LiMnO_2$ materials. This reaction route provides an alternative to the single-step reaction, and may be useful when employing starting oxides or salts (as the source of lithium,

25   manganese or dopant) which are difficult to react together to give a single-phase product under an inert atmosphere. Such oxides or salts may react more easily in air to give a doped oxidised lithium manganese oxide product, which can then be converted into the doped $LiMnO_2$ in inert atmosphere in a second stage.

30

It will be appreciated by those skilled in the art that doped oxidised lithium manganese oxide compounds can be formed by solid state reactions at temperatures ranging from 200 °C up to 900 °C, and that a range of temperature conditions could therefore be used in the first stage of this

5   process. The second, conversion step in inert atmosphere should preferably be performed at a higher temperature than the first step.

Example X

The two stage reaction process was used to prepare Al-doped $LiMnO_2$. Exact

10   stoichiometric amounts of lithium carbonate (99.9% pure), MnO_2 (99.0% pure) and theta-Al_2O_3 (99.95% pure) to give a product of formula $LiAl_{0.05}Mn_{0.95}O_2$ were mixed and ball-milled for 30 minutes. The resulting mixture was heated at 700°C in air for 8 hours, cooled, then fired at 1000 °C for 5 hours under a flow of zero grade nitrogen. The product was cooled over

15   a period of one hour, maintaining the nitrogen flow until the temperature dropped below 50 °C.

X-ray diffraction of the product after the first stage of the reaction in air (Figure 11A) showed a mixture of cubic spinel phase and Li_2MnO_3. The

20   presence of Li_2MnO_3 in this case is due to the amount of lithium, one mole of lithium per mole of manganese + aluminium, being too high for a single-phase spinel. The X-ray diffraction pattern of the product after the second stage under nitrogen (Figure 11B) shows complete conversion of the spinel and Li_2MnO_3 phases to $LiMnO_2$ product. The product is approximately 90%

25   monoclinic layered $LiMnO_2$, with around 10% o-$LiMnO_2$, practically identical to the $LiAl_{0.05}Mn_{0.95}O_2$ product of Example VI.

Electrodes and electrochemical cells containing the $LiAl_{0.05}Mn_{0.95}O_2$ material of this example were prepared as described in Example V, and the cells were

30   charged and discharged following the same procedures. Typical discharge capacities obtained at the 30 mA/g discharge rate are given for the 1st, 16th,

28

and 200th cycles at ambient and 55 °C in Table 8 in Example VIII. The electrochemical characteristics are almost identical to those of the $LiAl_{0.05}Mn_{0.95}O_2$ product of Example VI.

Example XI

The two-stage synthesis procedure described in Example IX was used to prepare a compound of stoichiometry $LiGa_{0.10}Mn_{0.90}O_2$. Exact stoichiometric amounts of lithium carbonate (99.9% pure), manganese carbonate (99.5% pure) and gallium oxide Ga_2O_3 (99.9% pure) to give a product of formula $Li_{0.5}Ga_{0.10}Mn_{0.90}O_2$ were mixed and ground in an acetone slurry using a mortar and pestle. The mixture was loaded into a vessel formed from an inert metal alloy and fired in a furnace at 700 °C for 20 hours in air. The X-ray diffraction pattern of the product, in Figure 12A, shows that it was a single phase cubic spinel with a unit cell parameter of $a = 8.227$ Å.

This compound was ground in acetone with an equivalent of lithium carbonate to give a product of formula $LiGa_{0.10}Mn_{0.90}O_2$, and heated under a flow of zero grade nitrogen at 1000 °C for 15 hours. The X-ray diffraction pattern of this product, in Figure 12B, shows 80% formation of monoclinic layered $LiMnO_2$, with unit cell parameters $a = 5.430$ Å, $b = 2.810$ Å, $c = 5.387$ Å, and $\beta = 115.78$ °. The remaining 20% of the product is o-$LiMnO_2$.

This result demonstrates that gallium may be used as an alternative, or in addition, to aluminium or chromium as a means of stabilising the layered monoclinic modification of $LiMnO_2$.

29

Example XII

The two-stage synthesis procedure described in Example IX was used to prepare compounds of stoichiometry $LiCr_{0.05}Ga_{0.05}Mn_{0.90}O_2$ and $LiCr_{0.05}B_{0.05}Mn_{0.90}O_2$. Exact stoichiometric amounts of lithium carbonate (99.9% pure), manganese carbonate (99.5% pure), Cr_2O_3 (99.9% pure) and gallium oxide Ga_2O_3 (99.9% pure) or boric acid H_3BO_3 (99.9% purity) to give products of formulae $Li_{0.5}Cr_{0.05}Ga_{0.05}Mn_{0.90}O_2$ and $Li_{0.5}Cr_{0.05}B_{0.05}Mn_{0.90}O_2$ were mixed and ground in an acetone slurry using a mortar and pestle. The mixtures were loaded into a vessel formed from an inert metal alloy and fired in a furnace at 700 °C for 20 hours in air. The X-ray diffraction patterns of the products in Figure 13A&C show that both were single phase cubic spinels with a unit cell parameter of $a = 8.227$ Å for the $Li_{0.5}Cr_{0.05}Ga_{0.05}Mn_{0.90}O_2$ material and $a = 8.234$ Å for the $Li_{0.5}Cr_{0.05}B_{0.05}Mn_{0.90}O_2$ material.

These compounds were each ground in acetone with an equivalent of lithium carbonate to give products of formulae $LiCr_{0.05}Ga_{0.05}Mn_{0.90}O_2$ and $LiCr_{0.05}B_{0.05}Mn_{0.90}O_2$, and heated under a flow of zero grade nitrogen at 1000°C for 15 hours. The X-ray diffraction patterns of the products in Figure 13B&D show the formation of phase-pure monoclinic layered $LiMnO_2$ in both cases, with unit cell parameters $a = 5.410$ Å, $b = 2.815$ Å, $c = 5.378$ Å, and $\beta = 115.79$ ° for the $LiCr_{0.05}Ga_{0.05}Mn_{0.90}O_2$ material, and $a = 5.429$ Å, $b = 2.811$ Å, $c = 5.380$ Å, and $\beta = 115.86$ ° for the $LiCr_{0.05}B_{0.05}Mn_{0.90}O_2$ material.

The above examples show that monoclinic layered $LiMnO_2$ may be formed during a high temperature solid state reaction involving metal doping, under specific conditions of time and temperature, and with appropriate starting reagents. Zero grade nitrogen is sufficient to control the manganese oxidation state in the formation of the monoclinic $LiMnO_2$ material, as only very little Li_2MnO_3 and no spinel phases were usually formed in the reactions under zero grade nitrogen.

30

The temperature window for producing layered monoclinic $LiMnO_2$ is in the range 800 to 1080°C.

The formation of aluminium doped layered monoclinic $LiMnO_2$ from lithium
5 carbonate, manganese oxide and aluminium oxide (or hydroxide) precursors by high temperature solid state reaction is facilitated by the inclusion of an additional metal, such as chromium.

It will be appreciated by those skilled in the art that the selection of reagents,
10 in particular their average particle sizes and reactivity, will influence the optimum conditions of time and/or temperature to achieve the preferred result. As shown in the examples, under appropriately selected conditions, the high temperature solid state reaction method of the invention can produce stable layered monoclinic $LiMnO_2$ doped with aluminium, chromium, gallium, or combinations of aluminium,
15 chromium, gallium and boron. Combinations of aluminium and chromium result in improved electrochemical properties over materials doped with aluminium alone. It is anticipated that other combinations may also result in improvements.

Where in the foregoing description reference has been made to specific
20 components or integers of the invention having known equivalents then such equivalents are herein incorporated as if individually set forth.

Although this invention has been described by way of example and with reference to possible embodiments thereof it is to be understood that modifications or
25 improvements may be made thereto without departing from the scope or spirit of the invention.

CLAIMS

1.　　A metal-doped lithium manganese oxide composition having the formula $LiM^1_{m1}M^2_{m2}...M^x_{mx}Mn_zO_2$ wherein M^1, M^2...M^x are each different metal ions, $m1+m2+...mx+z$ is substantially equal to 1, $m1+m2+...mx$ is greater than zero but less than 0.75 and z and at least m1 are greater than zero, providing that where m2...mx are zero M^1 is Cr and $0<m1<0.05$ or M^1 is Ga.

2.　　A composition according to claim 1 in predominantly monoclinic form.

3.　　A composition according to either claim 1 or claim 2 wherein M^1, M^2...M^x are each selected to have an ionic radius in their relevant oxidation state, similar to or less than that of Mn^{3+}.

4.　　A composition according to claim 3 wherein M^1, M^2...M^x are each selected from the group consisting of Al, Ga, Cr, Co, Fe, B, V, Ti and Ru.

5.　　A composition according to claim 4 wherein M^1 is Al.

6.　　A composition according to claim 5 wherein M^2 is selected from Ga, Cr, Co, Fe, B, V, Ti and Ru.

7.　　A composition according to claim 6 wherein M^2 is Cr.

8.　　A composition according to claim 1 wherein M^1, M^2...M^x each has the property of existing in a minimally distorted octahedral sphere of co-ordination.

9.　　A composition according to claim 1 wherein M^1, M^2...M^x each has a formal oxidation state of 3+.

10. A composition according to claim 1 wherein $m_1+m_2+...m_x$ is greater than zero but less than 0.25.

11. A composition according to claim 1 of the formula $LiAl_{m1}Cr_{m2}Mn_zO_2$, predominantly in monoclinic form, wherein $0<m1\leq0.05$, $0<m2\leq0.05$ and $0.90\leq z<1.0$.

12. A composition according to claim 11 wherein $m1=0.05$, $m2=0.05$ and $z=0.90$.

13. A composition according to claim 11 wherein $m1=0.02$, $m2=0.05$ and $z=0.93$.

14. A composition according to claim 1 of the formula $LiCr_{m1}Mn_zO_2$ predominantly in monoclinic form, wherein $0<m1<0.05$ and $0.95<z<1.0$.

15. A composition according to claim 14 wherein $m1=0.03$ and $z=0.97$.

16. A composition according to claim 14 wherein $m1=0.01$ and $z=0.99$.

17. A composition according to claim 1 of the formula $LiGa_{m1}Mn_zO_2$, predominantly in monoclinic form, wherein $0<m1\leq0.10$ and $0.9\leq z<1.0$.

18. A composition according to claim 1 of the formula $LiM^1_{m1}Cr_{m2}Mn_zO_2$ wherein M^1 is selected from Ga or B, m1 and m2 are each greater than zero but less than 0.1 and $0.9<z<1.0$.

19. A method of synthesising a metal-doped lithium manganese oxide composition having the formula $LiM^1_{m1} M^2_{m2}...M^x_{mx} Mn_z O_2$ wherein M^1, $M^2...M^x$ are each different metal ions, $m1+m2+...mx + z$ is substantially equal to 1, $m1+m2+...mx$ is greater than zero but less than 0.75, and z and at least

m1 are each greater than zero, providing that where m2...mx are zero and M^1 is Cr then $0<m1<0.05$, in stable monoclinic form by solid state reaction.

20.   A method according to claim 19, wherein the solid state reaction includes:

5

-   mixing reagents including a lithium compound, a manganese compound and at least one additional metal compound, each compound selected from an oxide, a hydroxide and/or a carbonate, and

10

-   heating the mixture in a reactor under inert atmosphere, to a temperature exceeding 800°C for at least 2 hours.

21.   A method according to claim 20 wherein the lithium compound is lithium carbonate.

15

22.   A method according to either claim 20 or claim 21 wherein the manganese compound is manganese oxide.

23.   A method according to claim 20 wherein the or each metal of the at least one

20   additional metal compound is selected to have a ionic radius in its relevant oxidation state, similar to or less than that of Mn^{3+}.

24.   A method according to claim 23 wherein the or each metal of the at least one additional metal compound is selected from the group consisting of Al, Ga,

25   Cr, Co, Fe, B, V, Ti and Ru.

25.   A method according to claim 24 wherein the at least one additional metal compound includes aluminium oxide and chromium oxide.

30   26.   A method according to claim 25 wherein the reagents are mixed in substantially stoichiometric amounts for the synthesis of $LiAl_xCr_yMn_zO_2$

34

wherein x+y+z=1 and x and y are each ≥0.01 but ≤0.05 and z is ≥0.90 and ≤0.98.

27.   A method according to claim 24 wherein the at least one additional metal compound includes aluminium oxide.

28.   A method according to claim 27 wherein the aluminium oxide is a transitional alumina.

29.   A method according to claim 27 or claim 28 wherein the reagents are mixed in substantially stoichiometric amounts for the synthesis of $LiAl_xMn_yO_2$ wherein x+y=1, $0.01 \leq x \leq 0.10$ and $0.90 \leq y \leq 0.99$.

30.   A method according to claim 24 wherein the at least one additional metal compound includes chromium oxide.

31.   A method according to claim 30 wherein the reagents are mixed in substantially stoichiometric amounts for the synthesis of $LiCr_xMn_yO_2$, wherein x+y=1, $0.01 \leq x < 0.05$ and $0.95 < y \leq 0.99$.

32.   A method according to claim 20 wherein the or each metal of the at least one additional metal compound has a formal oxidation state of 3^+.

33.   A method according to any one of claims 20 to 32 further including the step of ball-milling the mixed reagents.

34.   A method according to any one of claims 20 to 33 wherein the mixture is heated to a temperature in the range substantially 900°C to 1080°C.

35.   A method according to claim 34 wherein the mixture is heated to a temperature of substantially 1000°C to 1080°C for a period of at least 5 hours.

35

36. A method according to any one of claims 20 to 35 wherein the inert atmosphere has a sufficiently low pO_2 to facilitate the formation of manganese in its 3+ oxidation state.

37. A method according to claim 36 wherein the pO_2 is substantially 10^{-5} atm or less.

38. A method according to claim 20 wherein the mixture is heated in a reactor having a high temperature stable lining.

39. A method of synthesising a metal-doped lithium manganese oxide composition of the formula $LiM^1_{m1}M^2_{m2}...M^x_{mx}Mn_2O_2$ wherein M^1, $M^2...M^x$ are each different metal ions, $m1+m2+...mx+z$ is substantially equal to 1, $m1+m2+...mx$ is greater than zero but less than 0.75 and z and at least m1 are each greater than zero, in stable predominantly monoclinic form, the method including the steps of:

- mixing reagents including a lithium compound, a manganese compound and at least one additional metal compound, each compound selected from an oxide, a hydroxide and/or a carbonate,

- heating the mixture in air to a temperature $\geq 200°C$ for at least 5 hours to produce oxygen-rich lithium manganese oxides,

- further heating the mixture in a reactor under inert atmosphere to a temperature exceeding 800°C for at least 2 hours.

40. A method according to claim 39 wherein the lithium compound is lithium carbonate.

41. A method according to either claim, 39 or claim 40 wherein the manganese compound is manganese carbonate.

42. A method according to claim 41 wherein the or each metal of the at least one additional metal compound is selected to have an ionic radius in its relevant oxidation state similar to or less than that of Mn^{3+}.

43. A method according to claim 42 wherein the or each additional metal compound is selected from Al, Ga, Cr, Co, Fe, B, V, Ti and Ru.

44. A method according to claim 43 wherein the or each additional metal compound includes at least one of an oxide of Cr, Al, Ga and B.

45. A method according to claim 39 wherein the or each additional metal compound has a formal oxidation state of 3^+.

46. A method according to any one of claims 39 to 45 wherein the heating in air is at a temperature in the range 600 to 850°C.

47. A method according to claim 46 wherein the heating in air is at substantially 700°C.

48. A method according to any one of claims 39 to 47 wherein the heating under inert atmosphere is at a temperature of substantially 1000-1080°C.

49. A method according to claim 48 wherein the inert atmosphere has a sufficiently low pO_2 to facilitate the formation of manganese in its 3+ oxidation state.

50. A method according to claim 48 wherein the reagents are mixed in substantially stoichiometric amounts for the synthesis of $LiCr_{0.05}Mn_{0.95}O_2$.

51.   A method according to claim 48 wherein the reagents are mixed in substantially stoichiometric amounts for the synthesis of $LiAl_{0.05}Mn_{0.95}O_2$.

5   52.   A method according to claim 48 wherein the reagents are mixed in substantially stoichiometric amounts for the synthesis of $LiM^1_{0.05}Cr_{0.05}Mn_{0.90}O_2$ wherein M^1 is selected from Al, Ga or B.

53.   A method according to claim 48 wherein the reagents are mixed in
10   substantially stoichiometric amounts for the synthesis of $LiGa_{0.1}Mn_{0.9}O_2$.

54.   An electrode material for a battery, said material including a composition according to any one of claims 1 to 18.

15   55.   A non-aqueous electrolyte lithium secondary battery including a positive electrode, a negative electrode capable of absorbing and desorbing lithium in a reversible manner and a lithium ion conducting non-aqueous electrolyte, wherein the positive electrode includes a composition according to any one of claims 1 to 18.

20

56.   Use of a composition according to any one of claims 1 to 18 in the manufacture of a non-aqueous electrolyte lithium secondary battery.

57.   A metal-doped lithium manganese oxide composition substantially as herein
25   described and with reference to the accompanying Examples.

58.   A method of synthesising a metal-doped lithium manganese oxide composition substantially as herein described and with reference to the accompanying Examples.

30
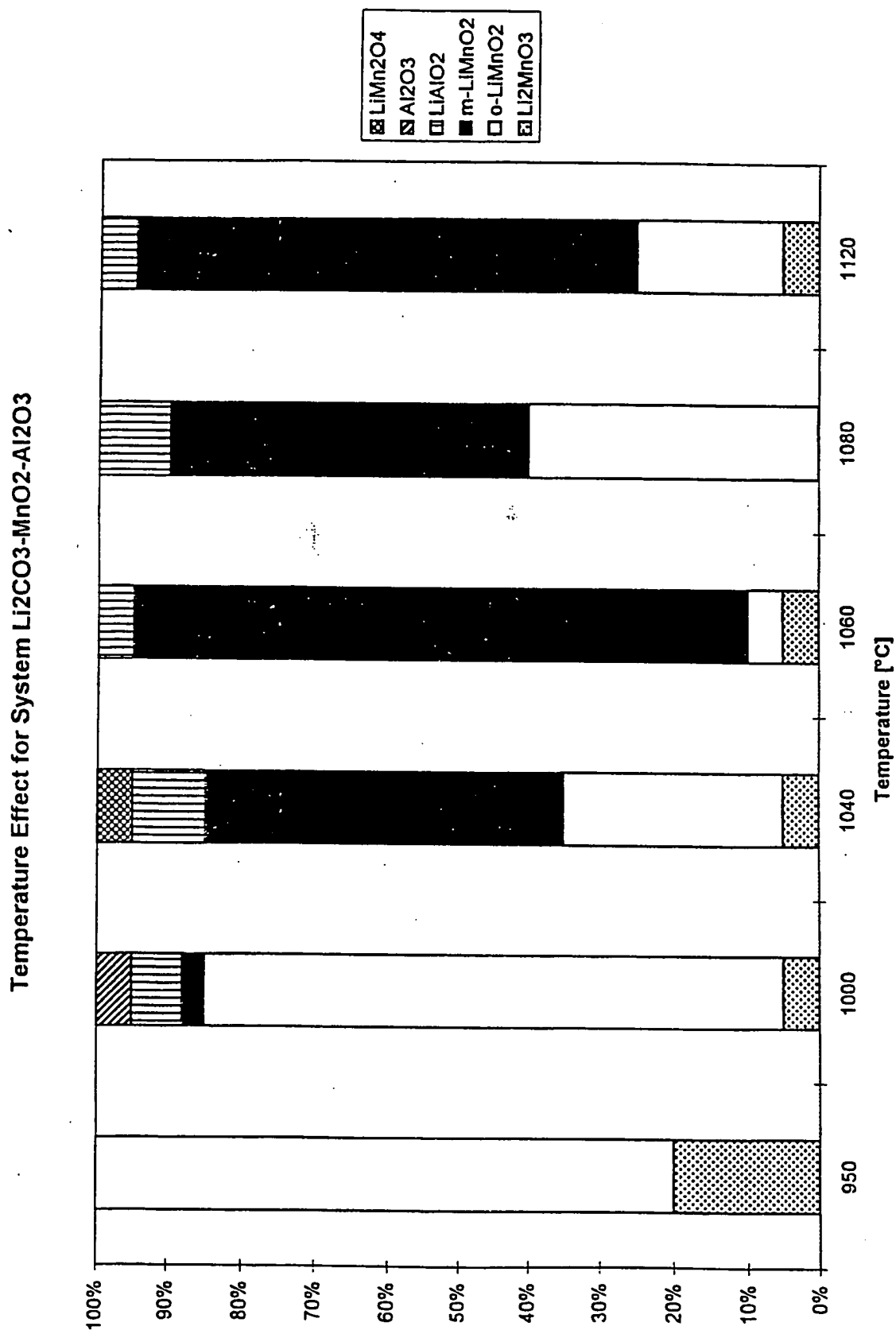
FIGURE 1

Time Effect for System Li2CO3-MnO2-Al2O3
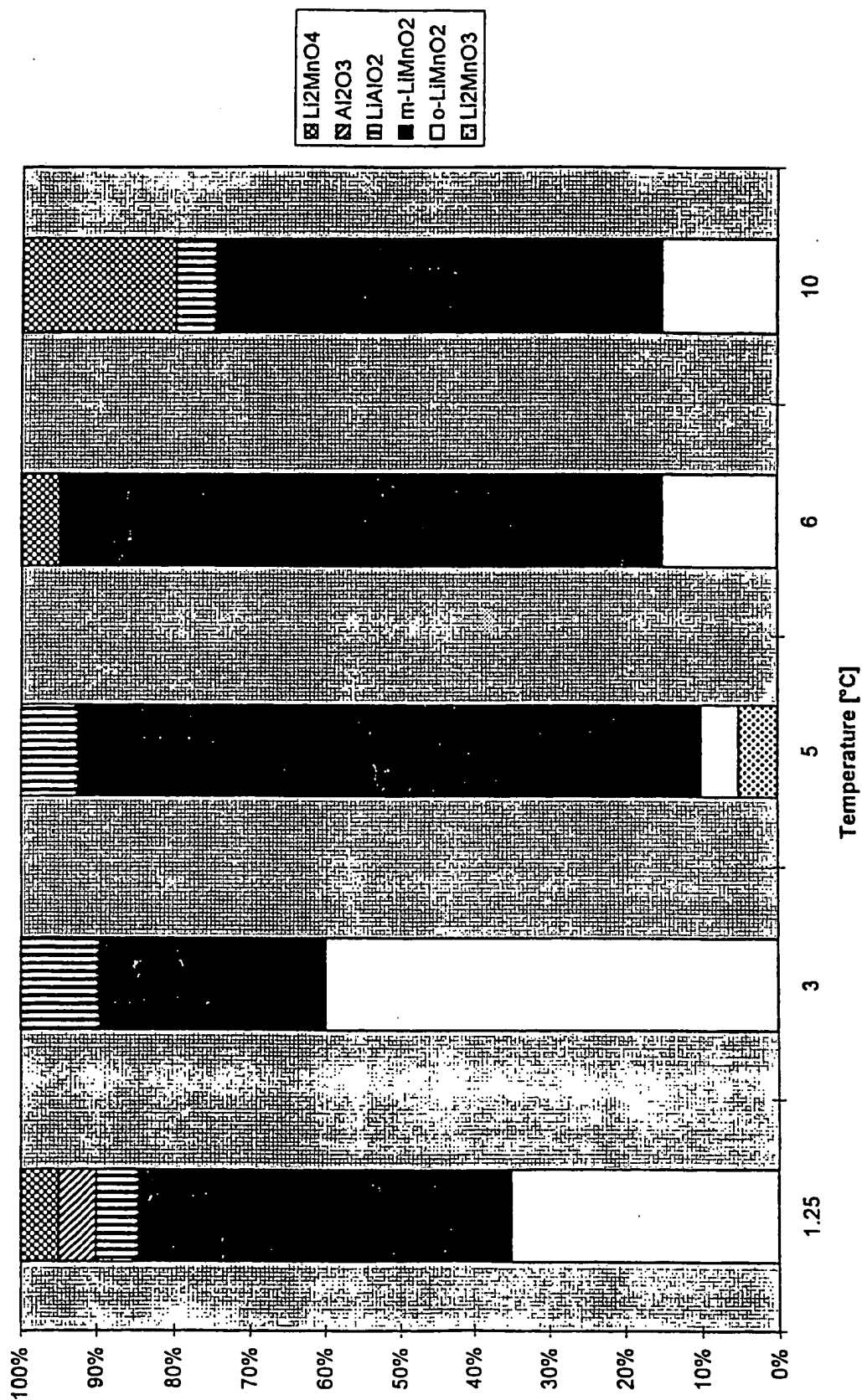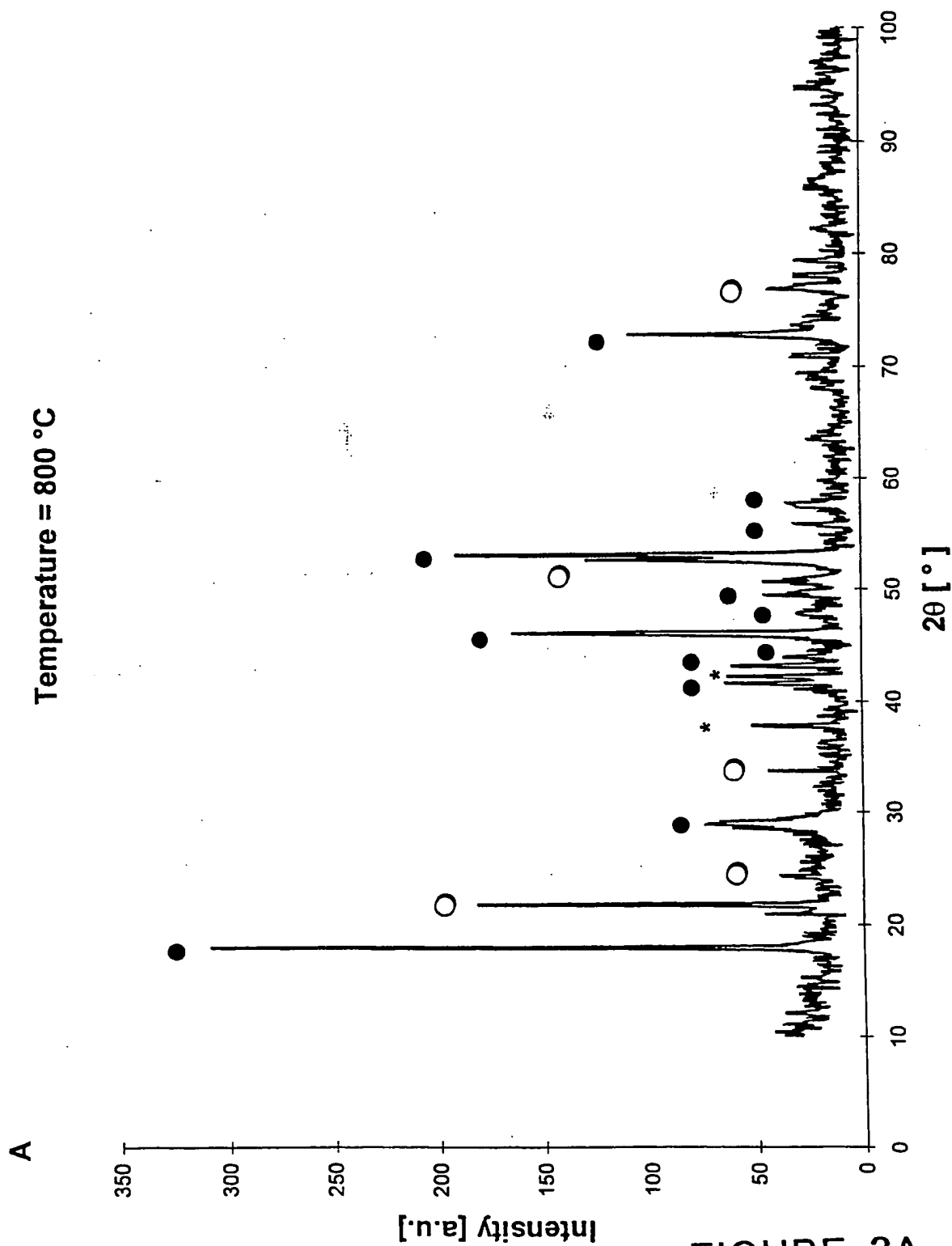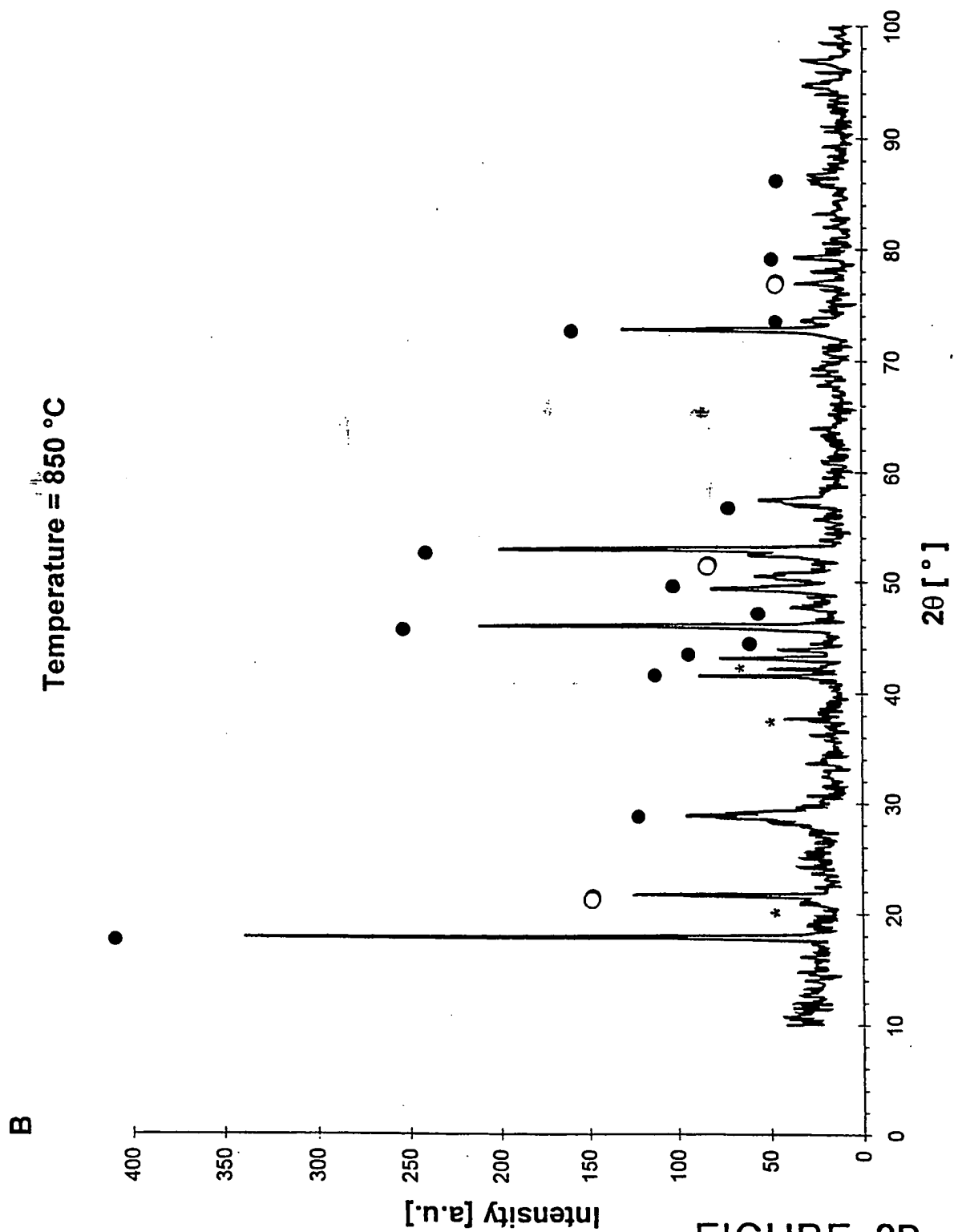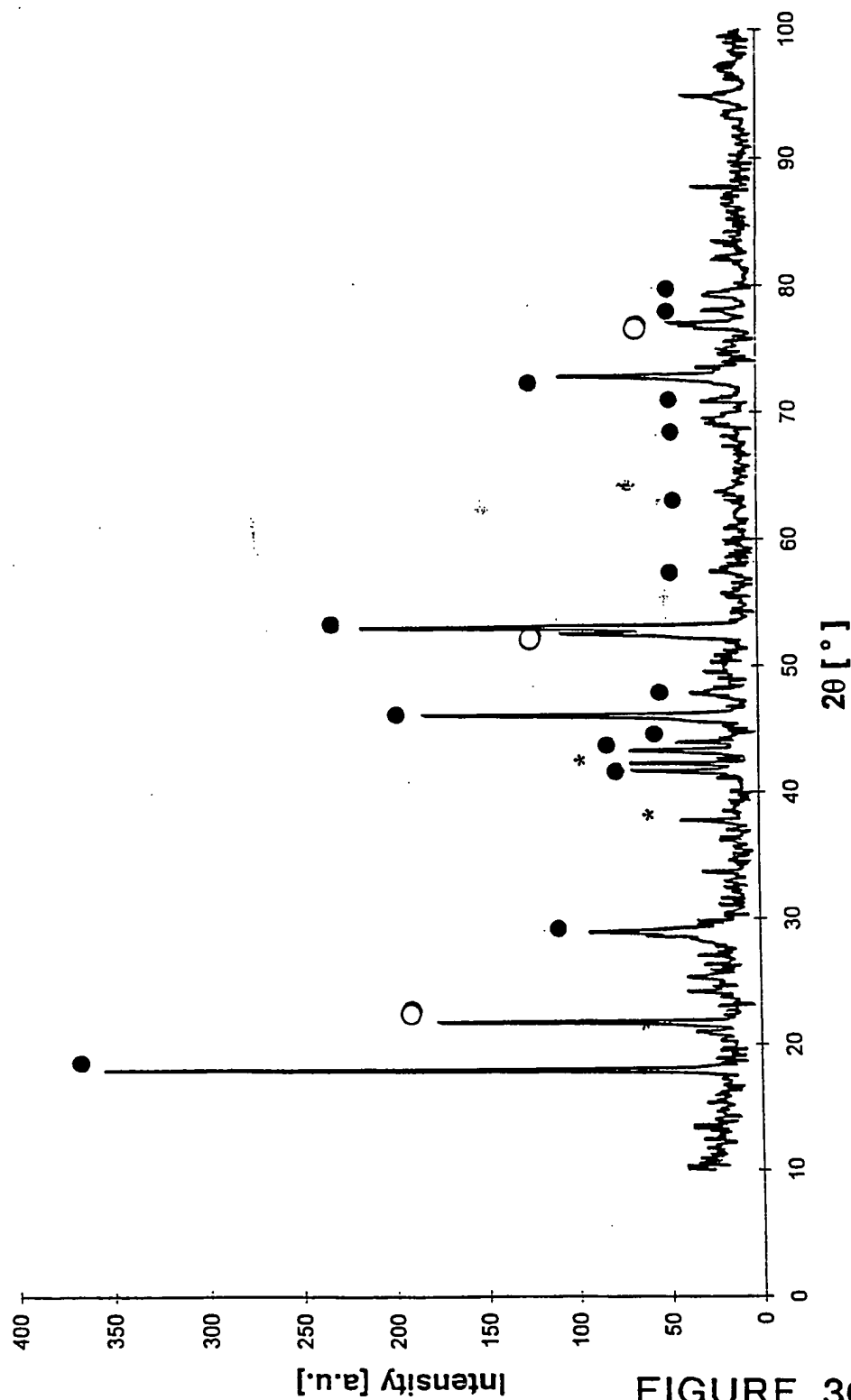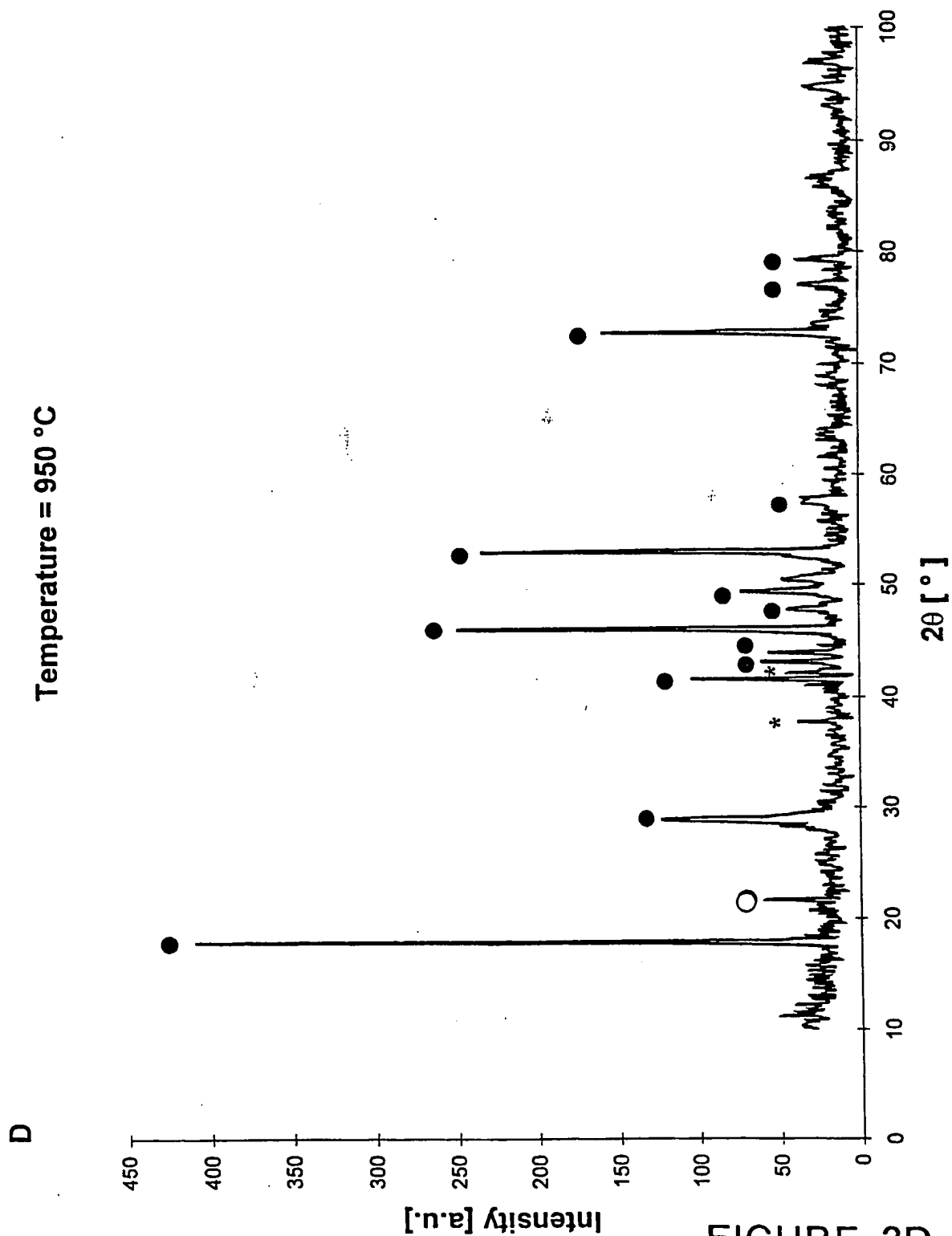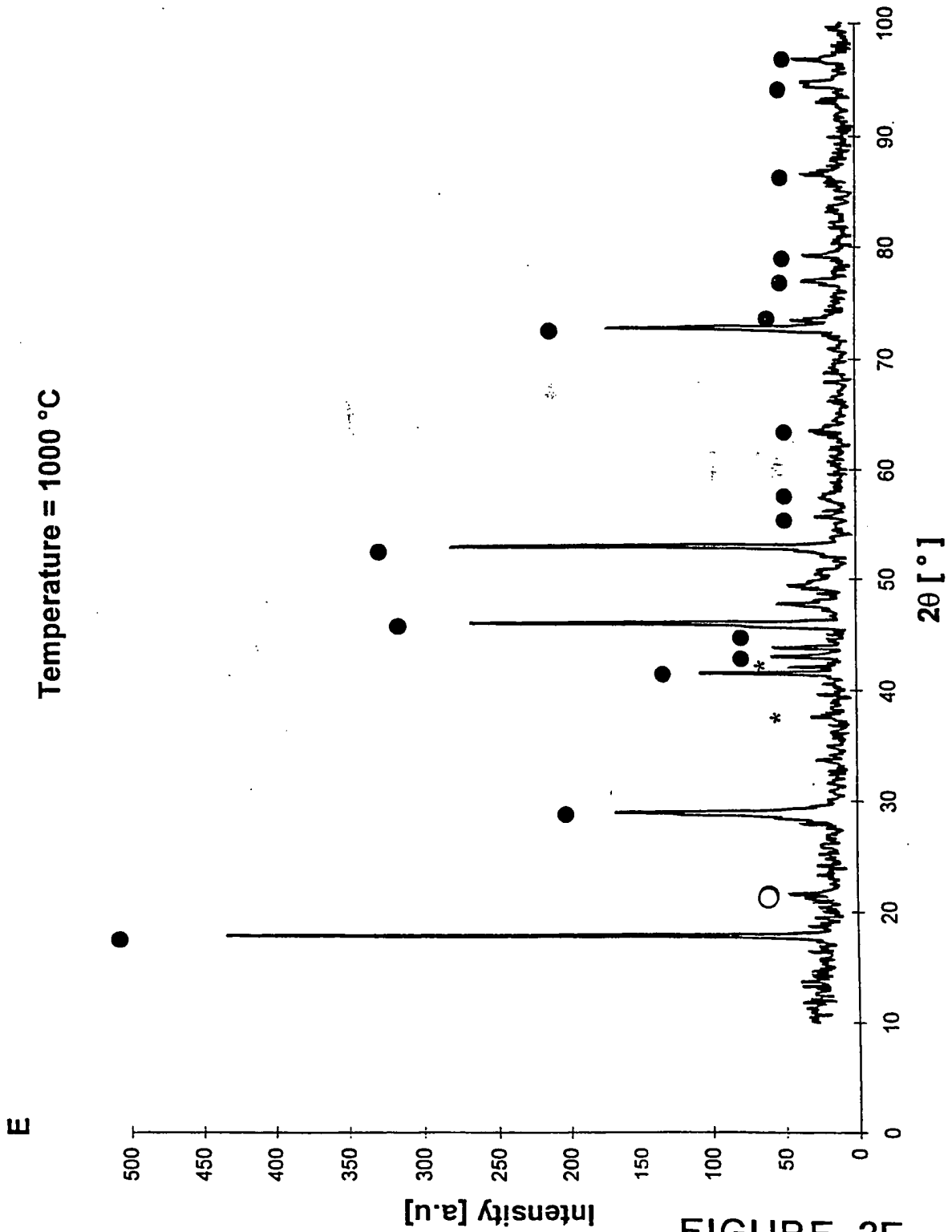
Legend:
- Li2MnO4
- Al2O3
- LiAlO2
- m-LiMnO2
- o-LiMnO2
- Li2MnO3

Temperature [°C]
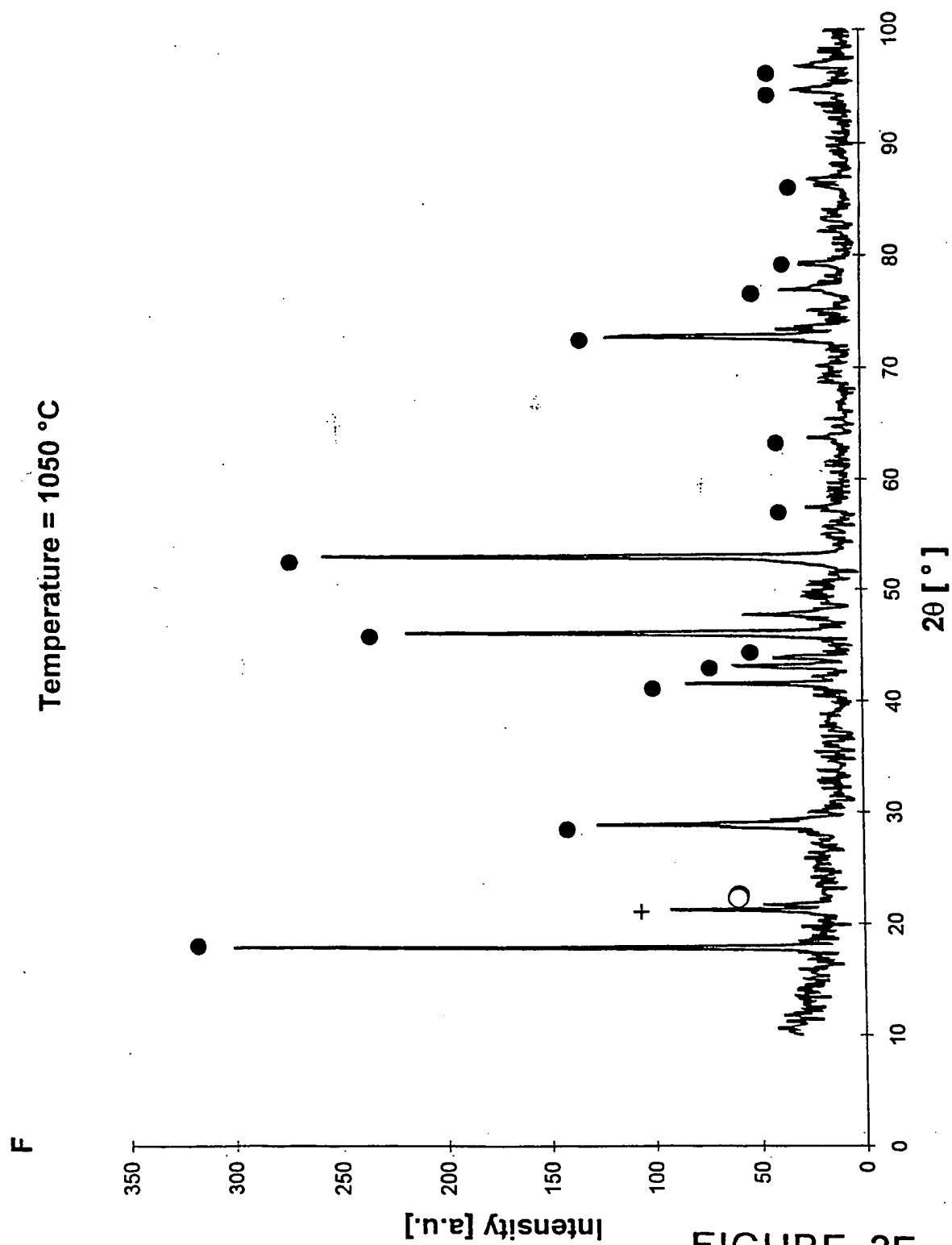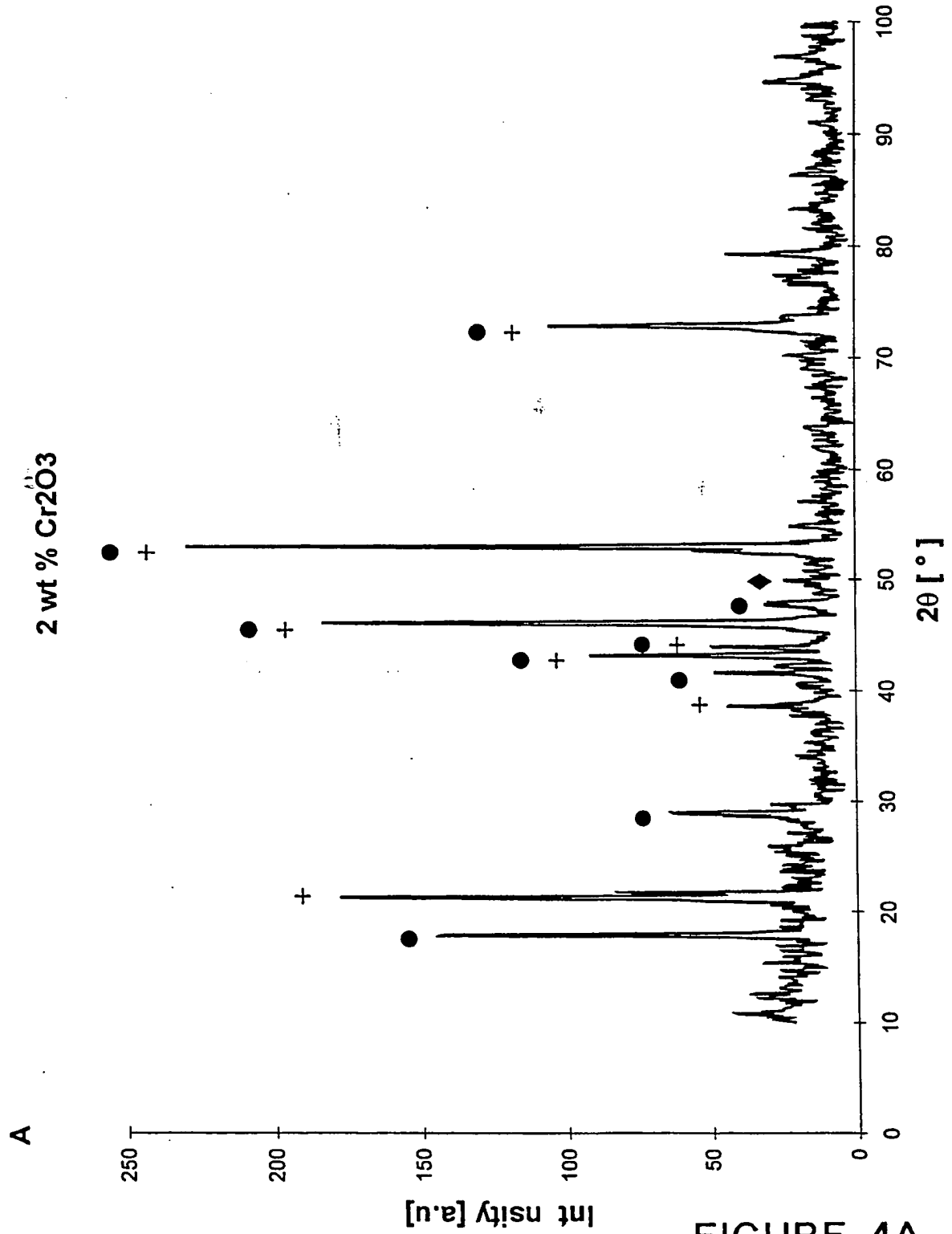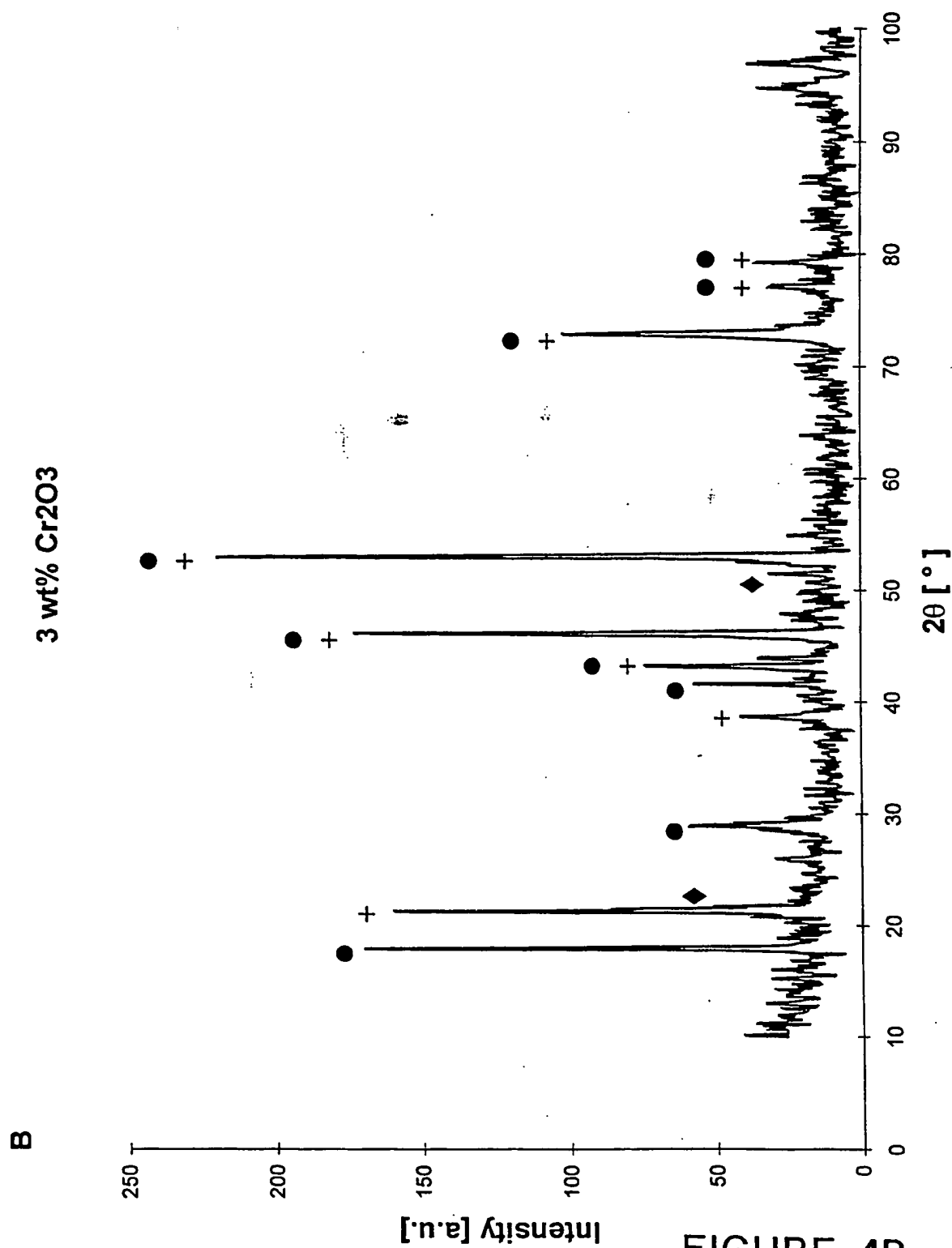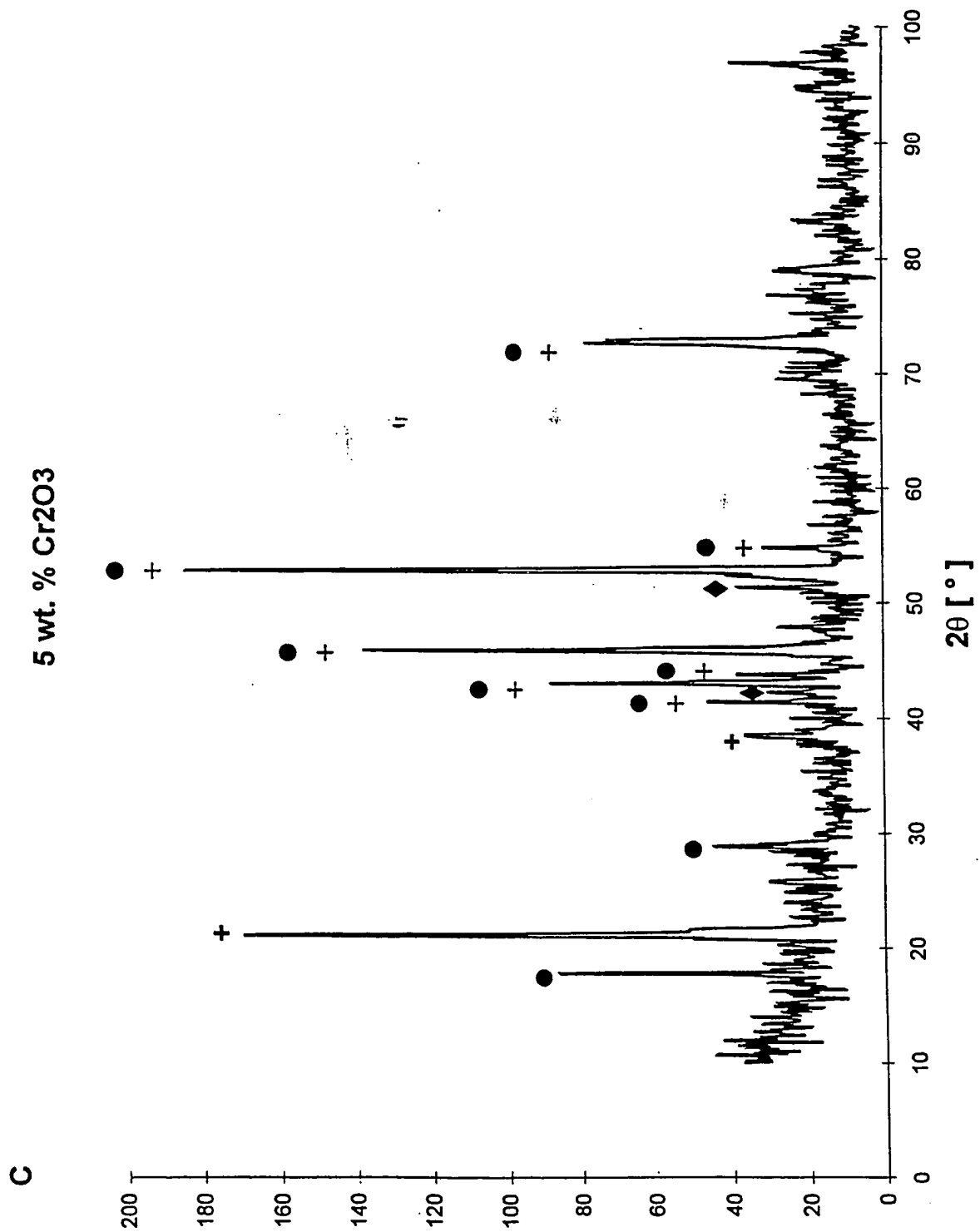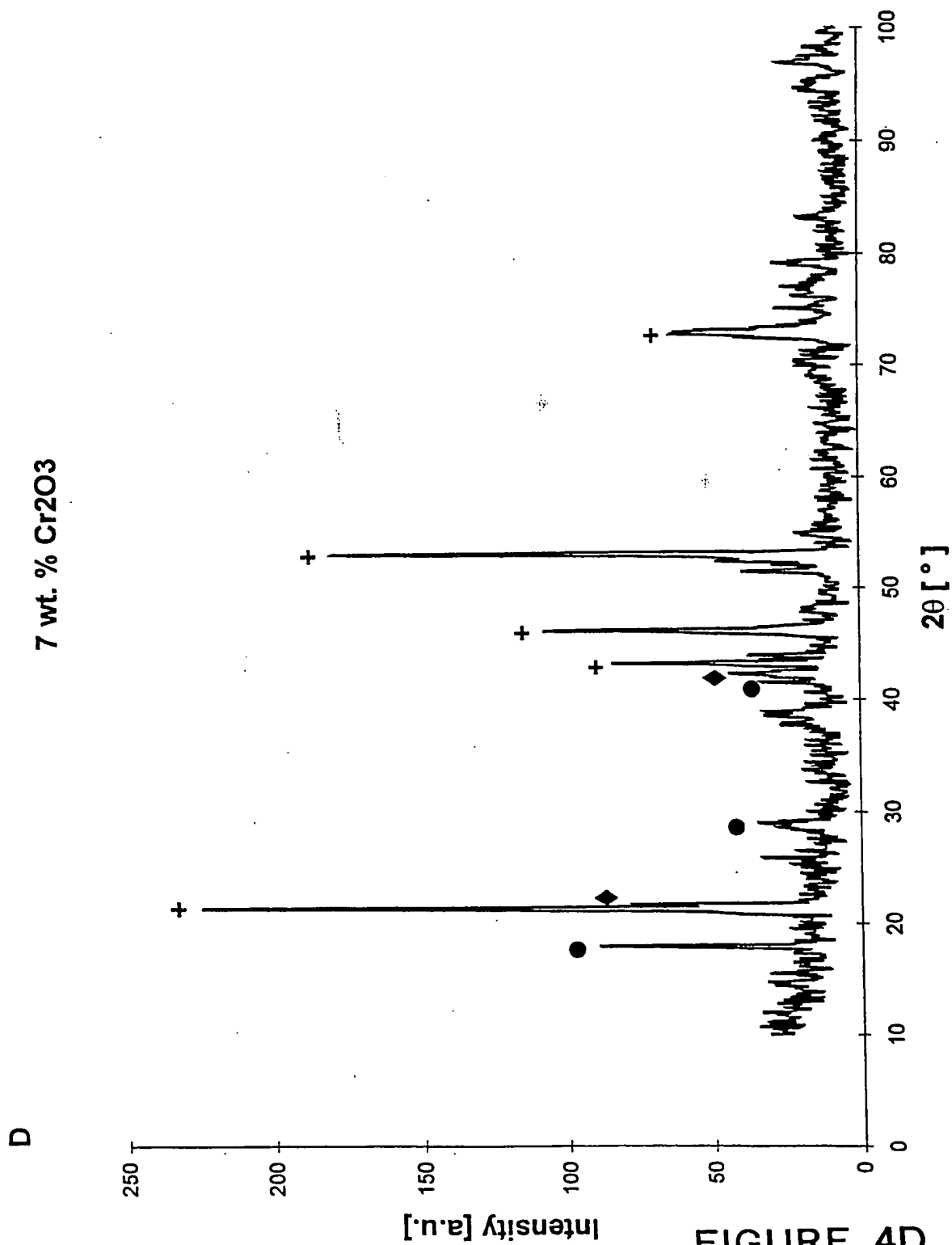
FIGURE 2
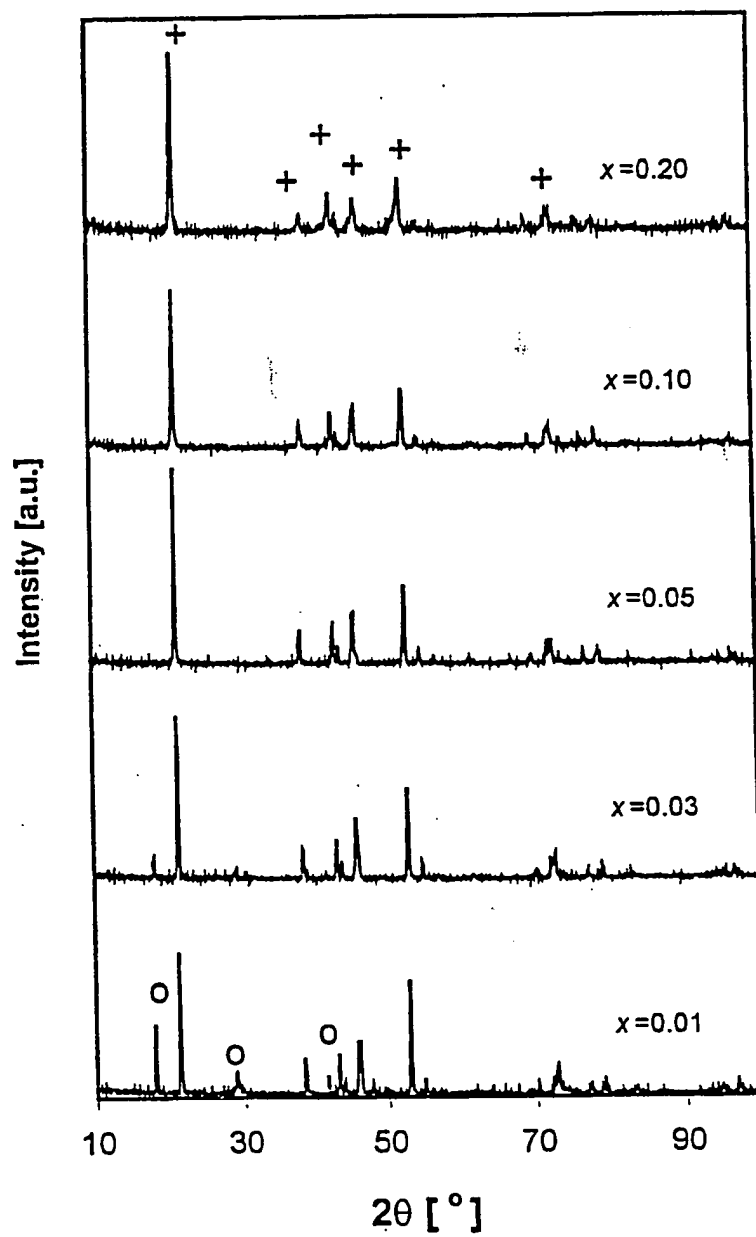
FIGURE 3A
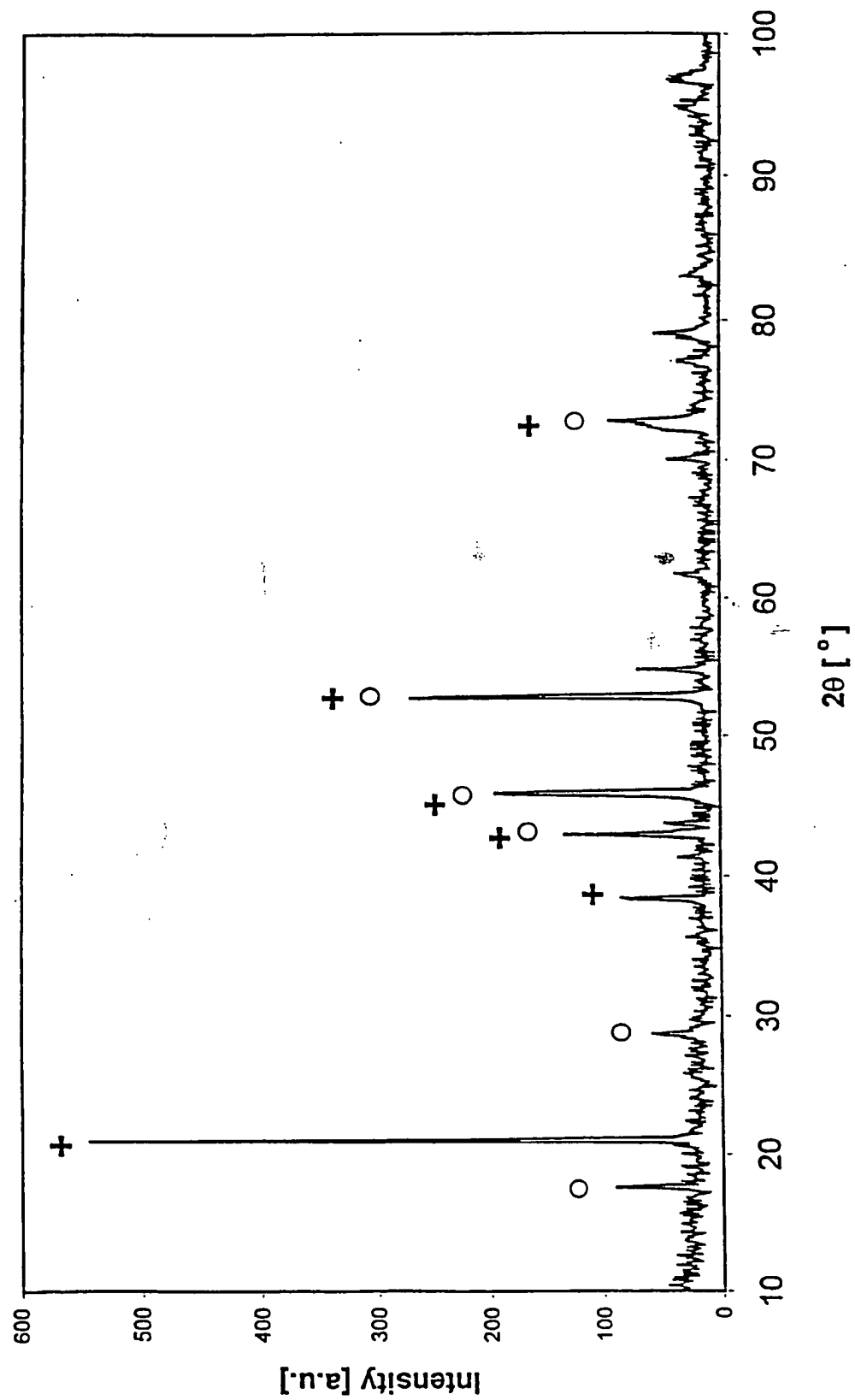
FIGURE 3B

FIGURE 3C
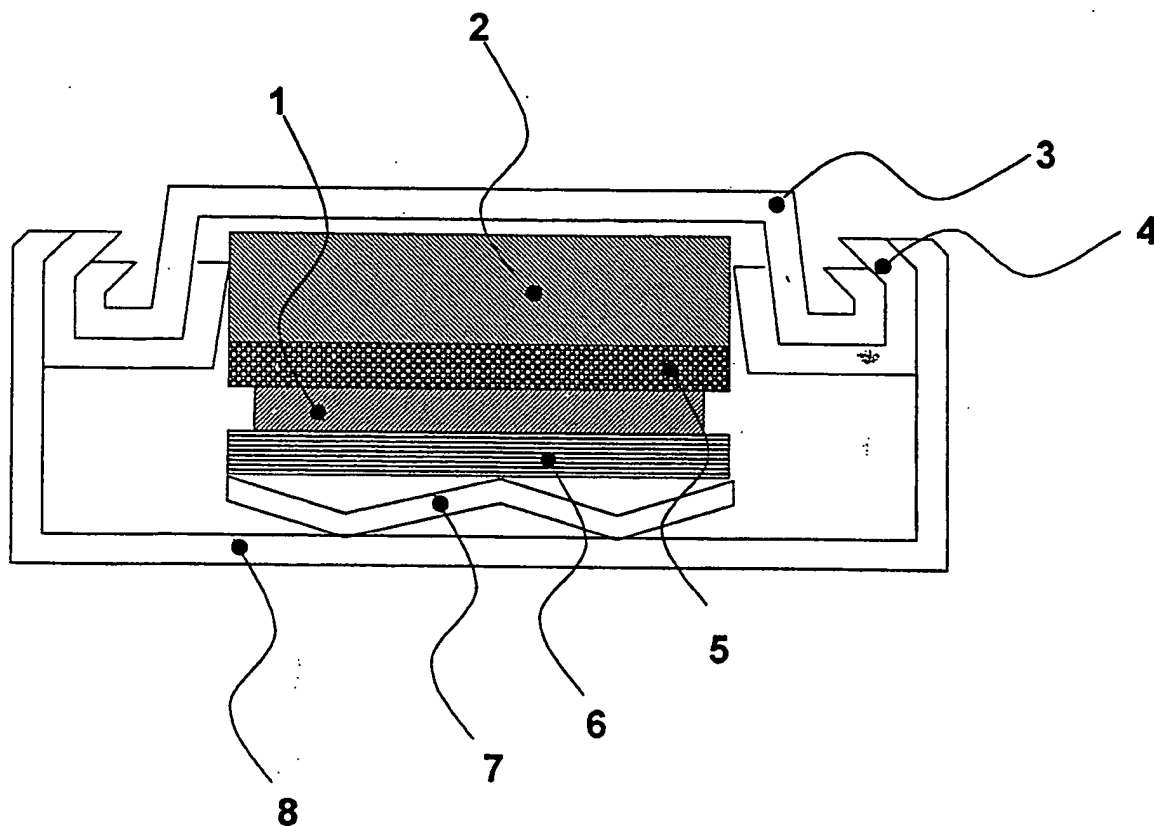
FIGURE 3D
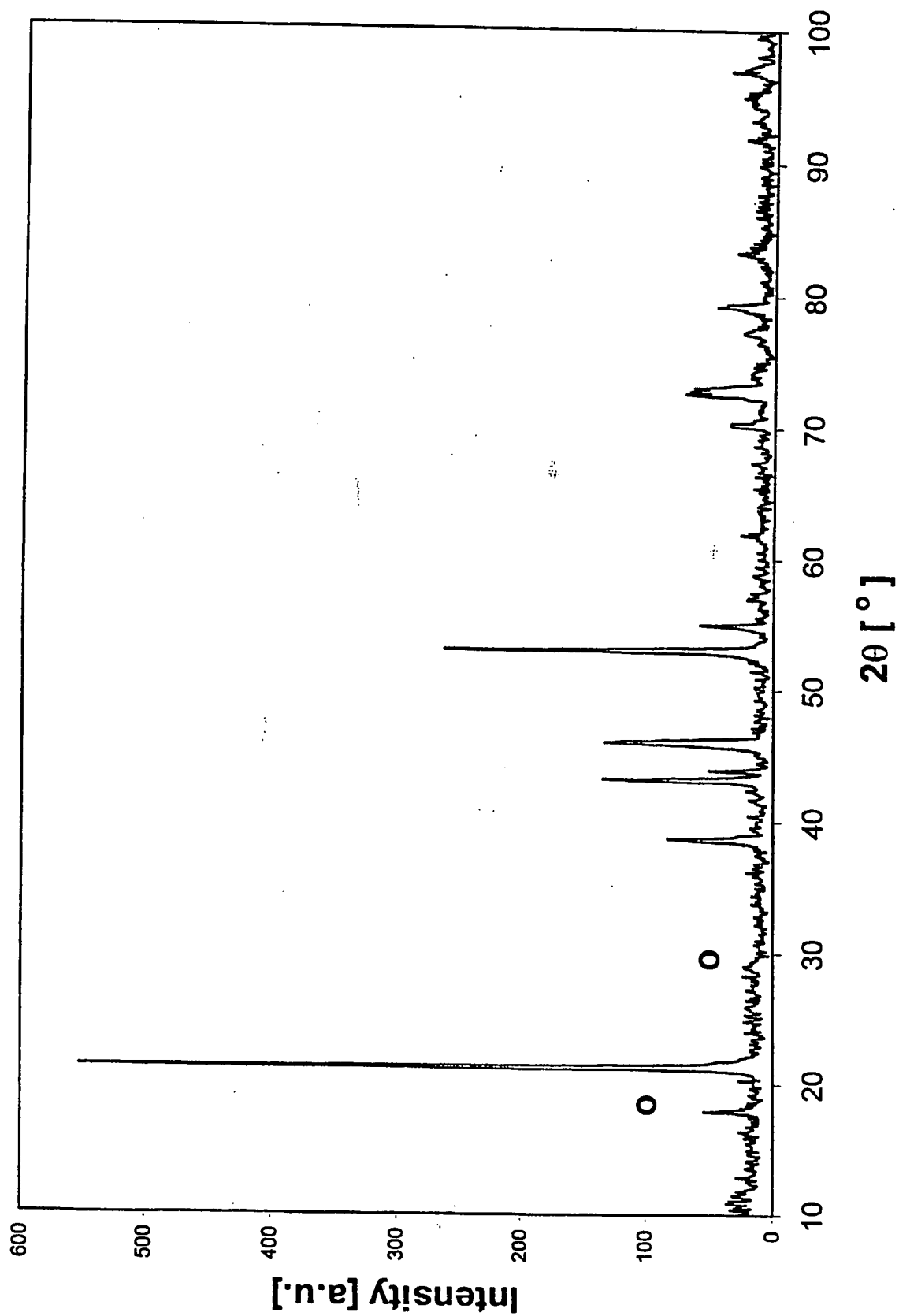
FIGURE 3E
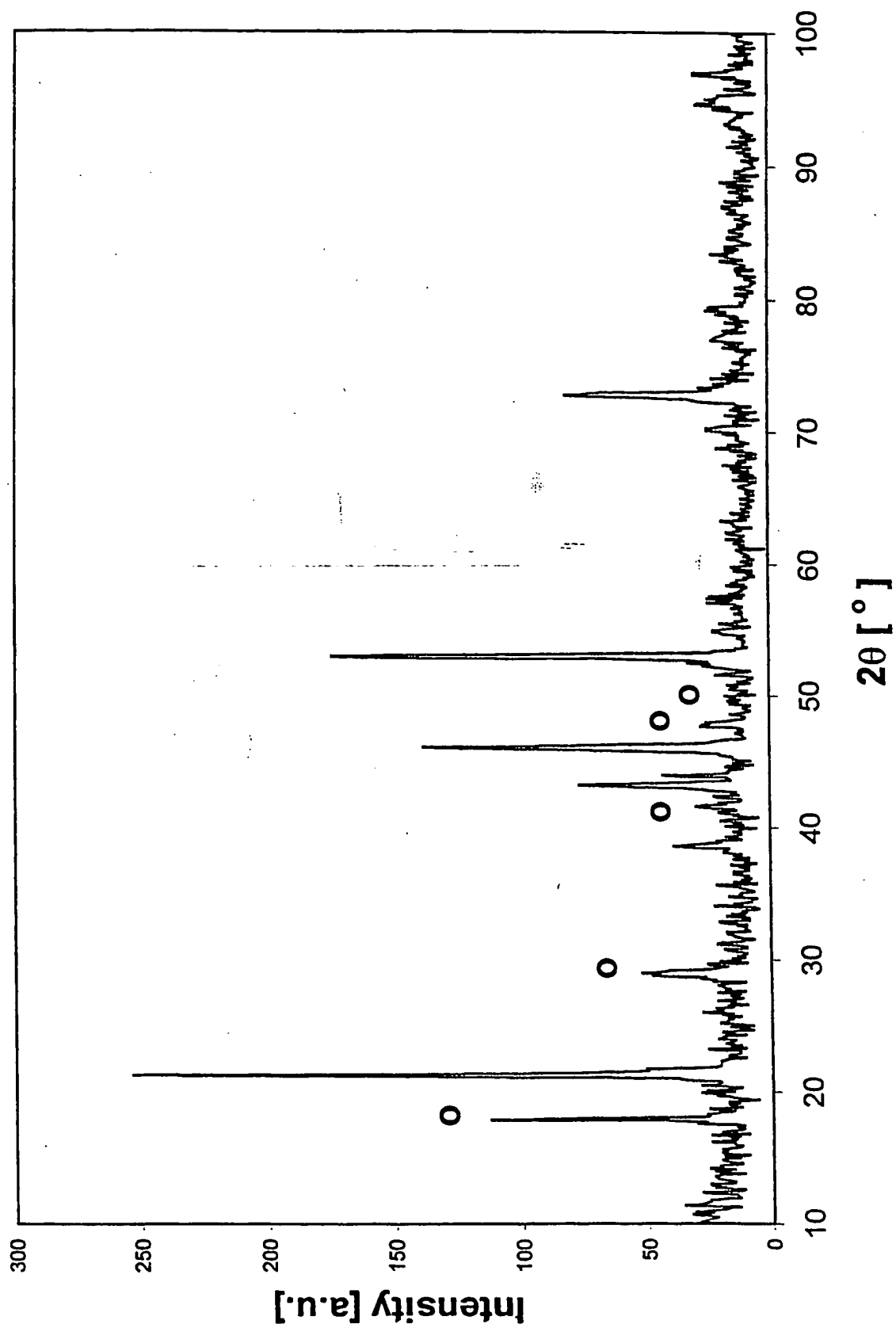
FIGURE 3F

FIGURE 4A
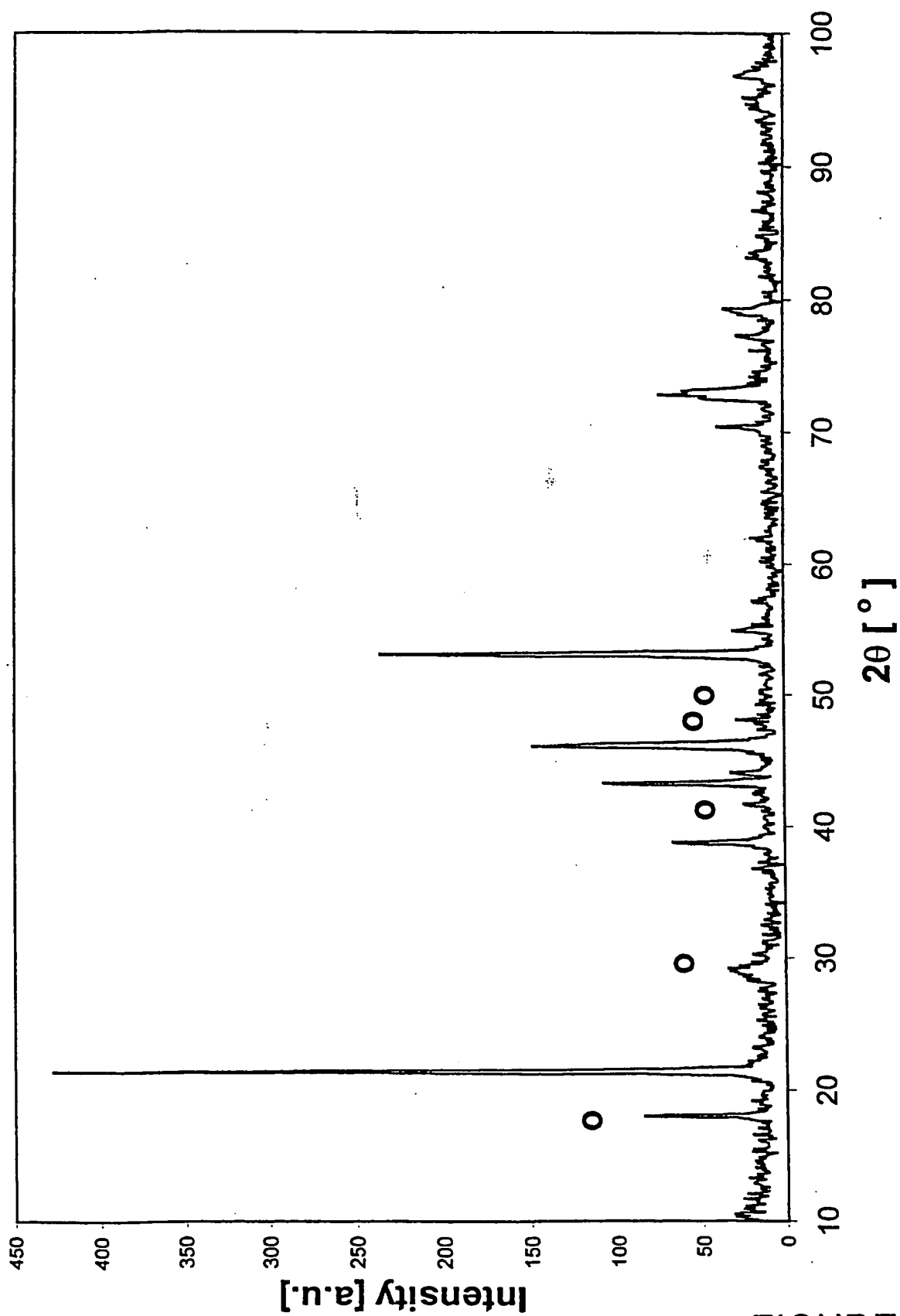
FIGURE 4B
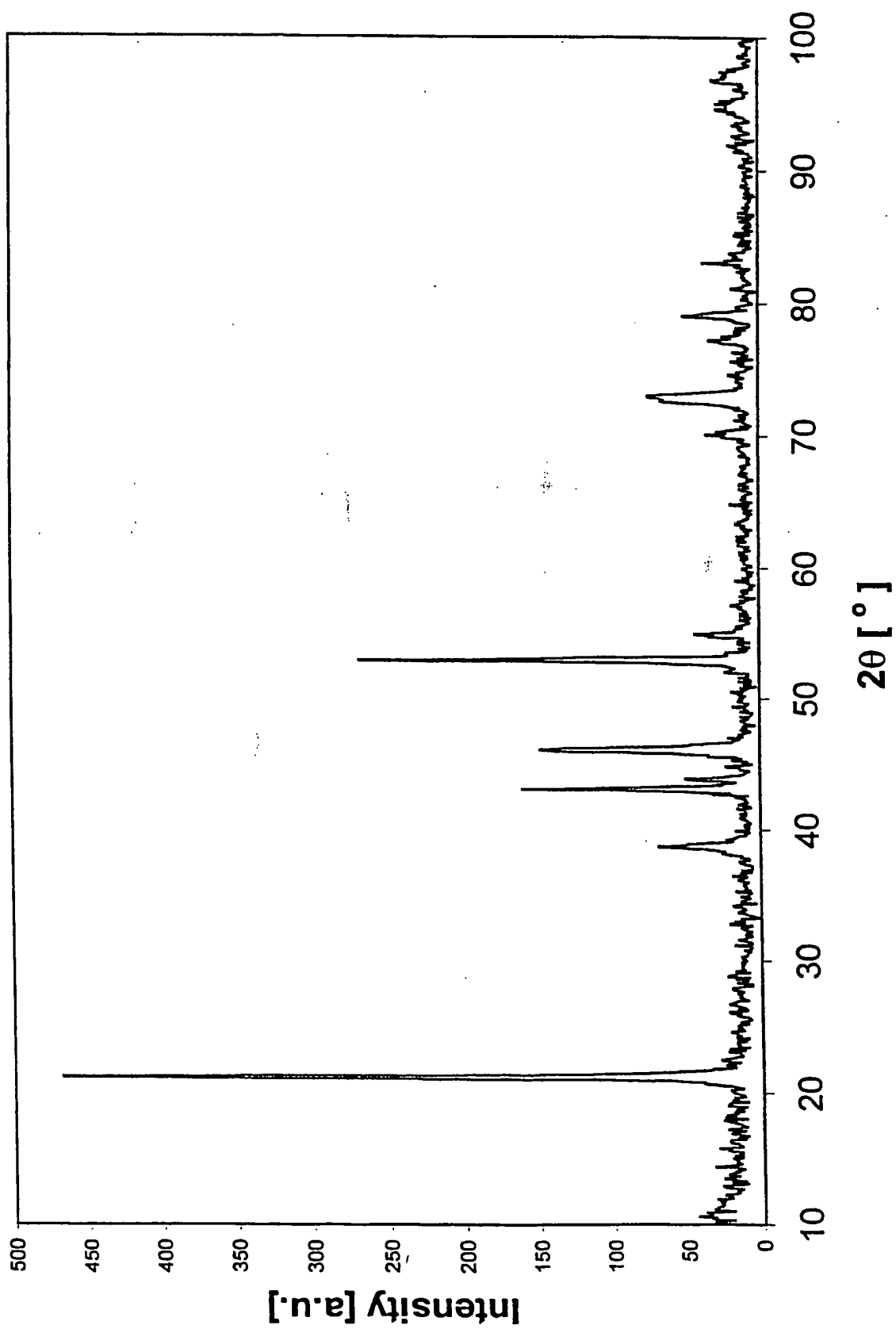
FIGURE 4C

FIGURE 4D
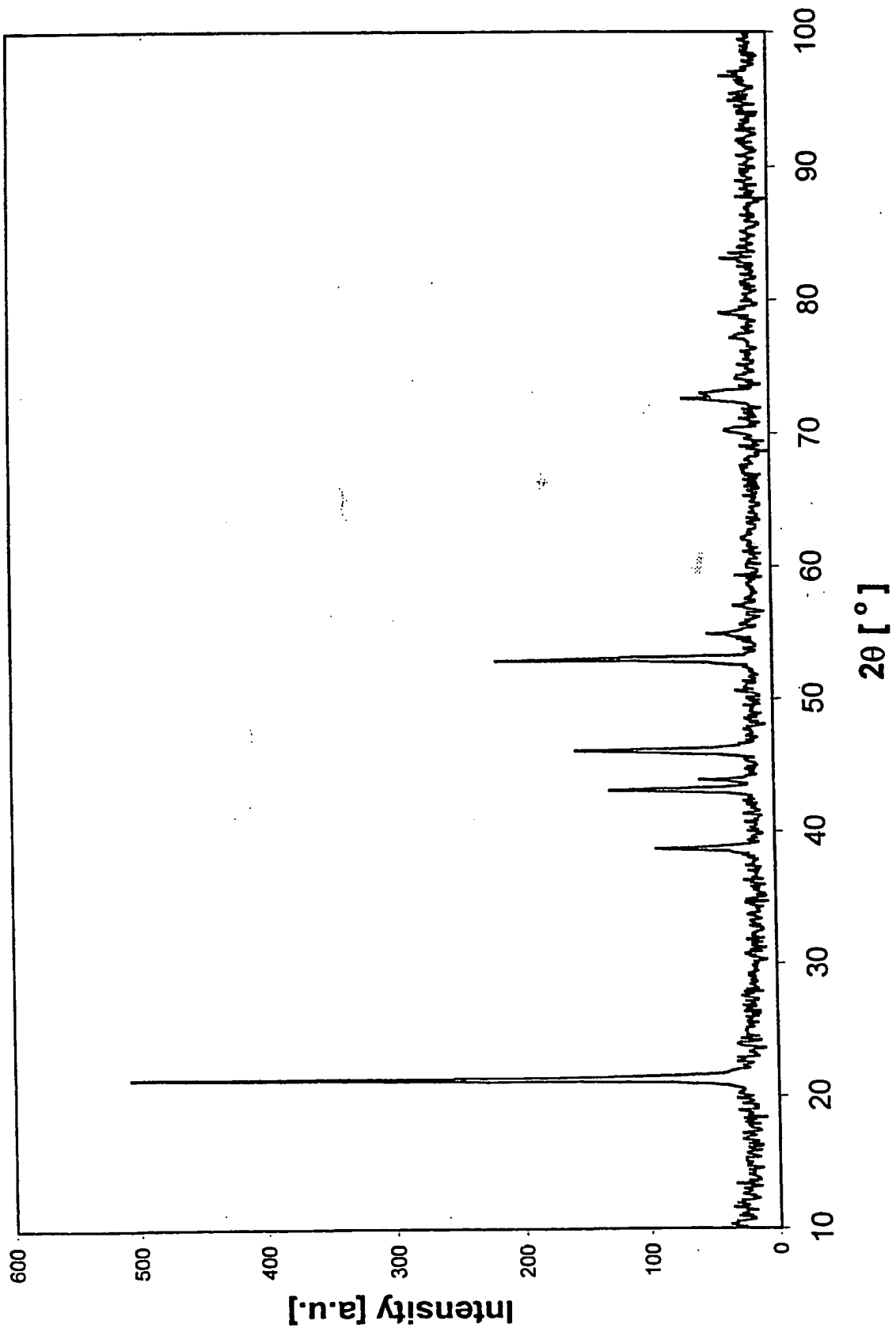
FIGURE 5

FIGURE 6
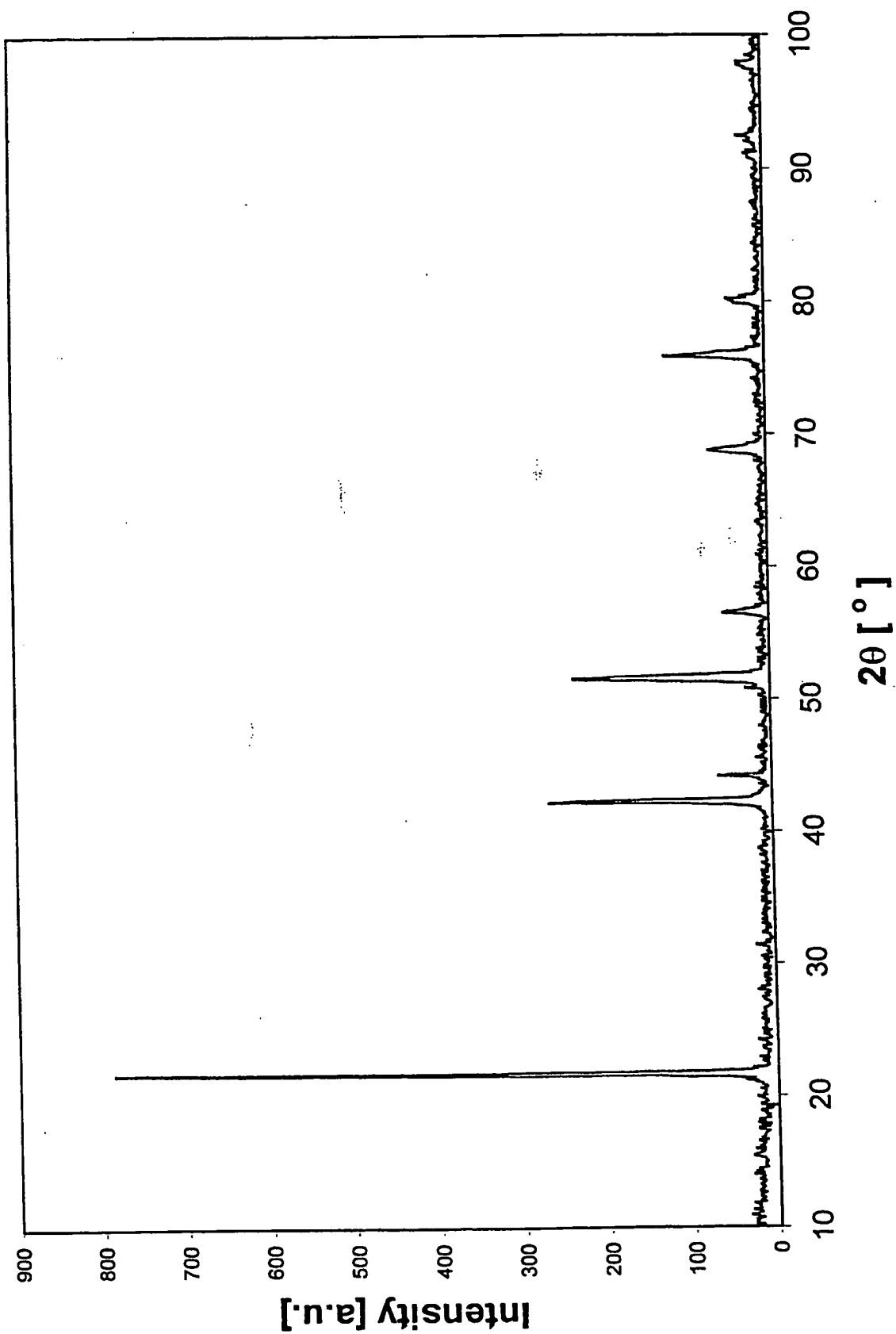
FIGURE 7
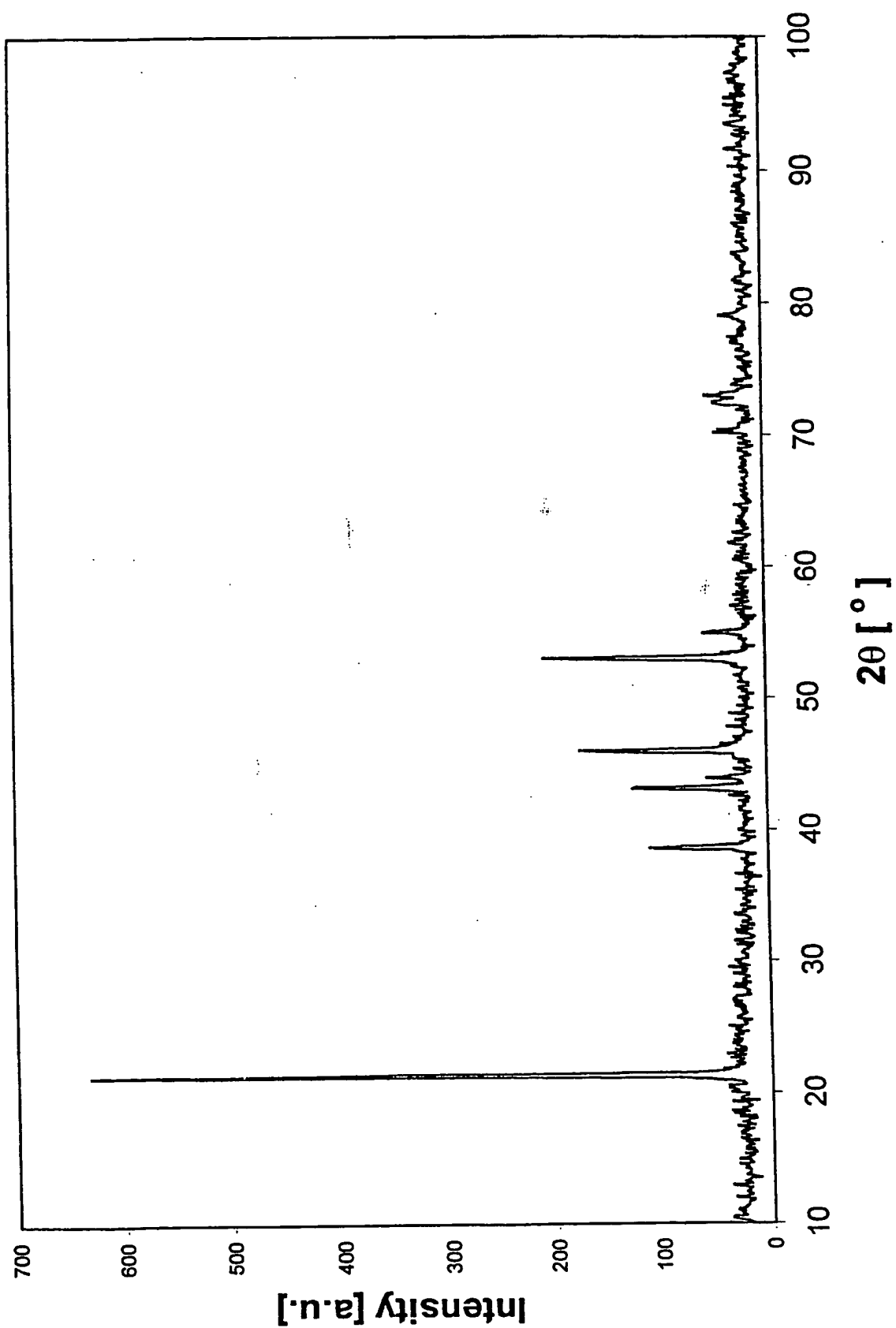
FIGURE 8

FIGURE 9A
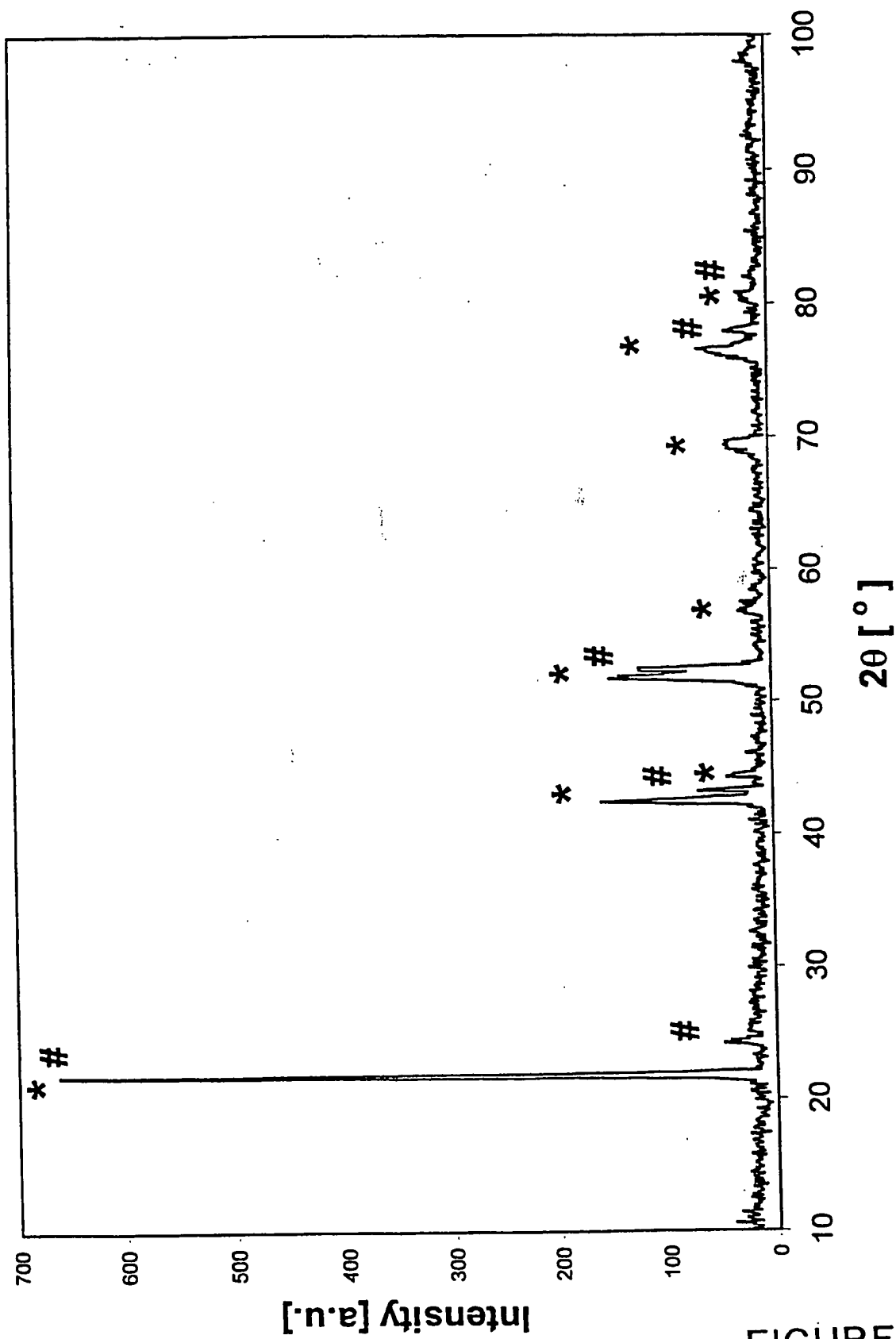
FIGURE 9B

FIGURE 9C
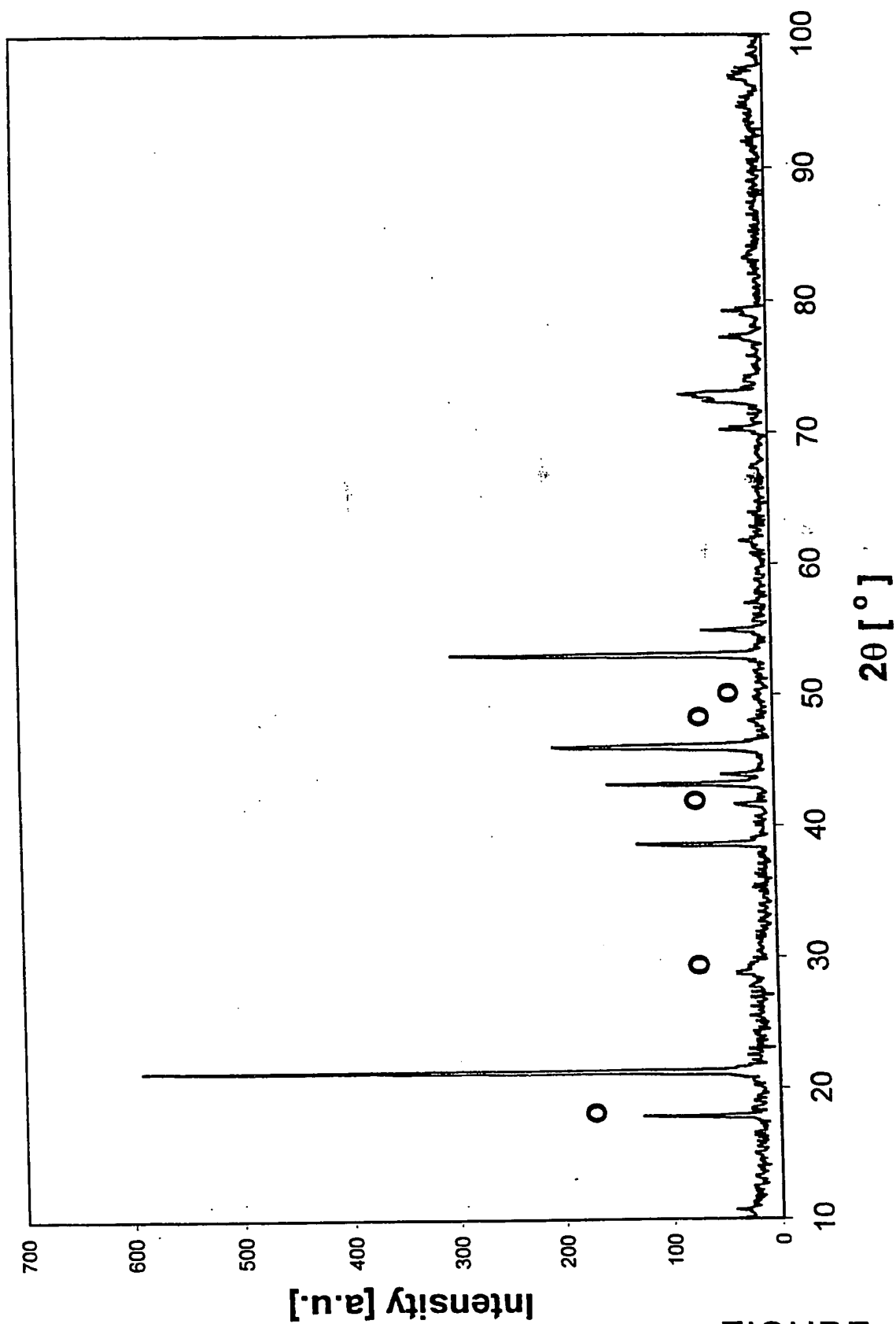
FIGURE 9D
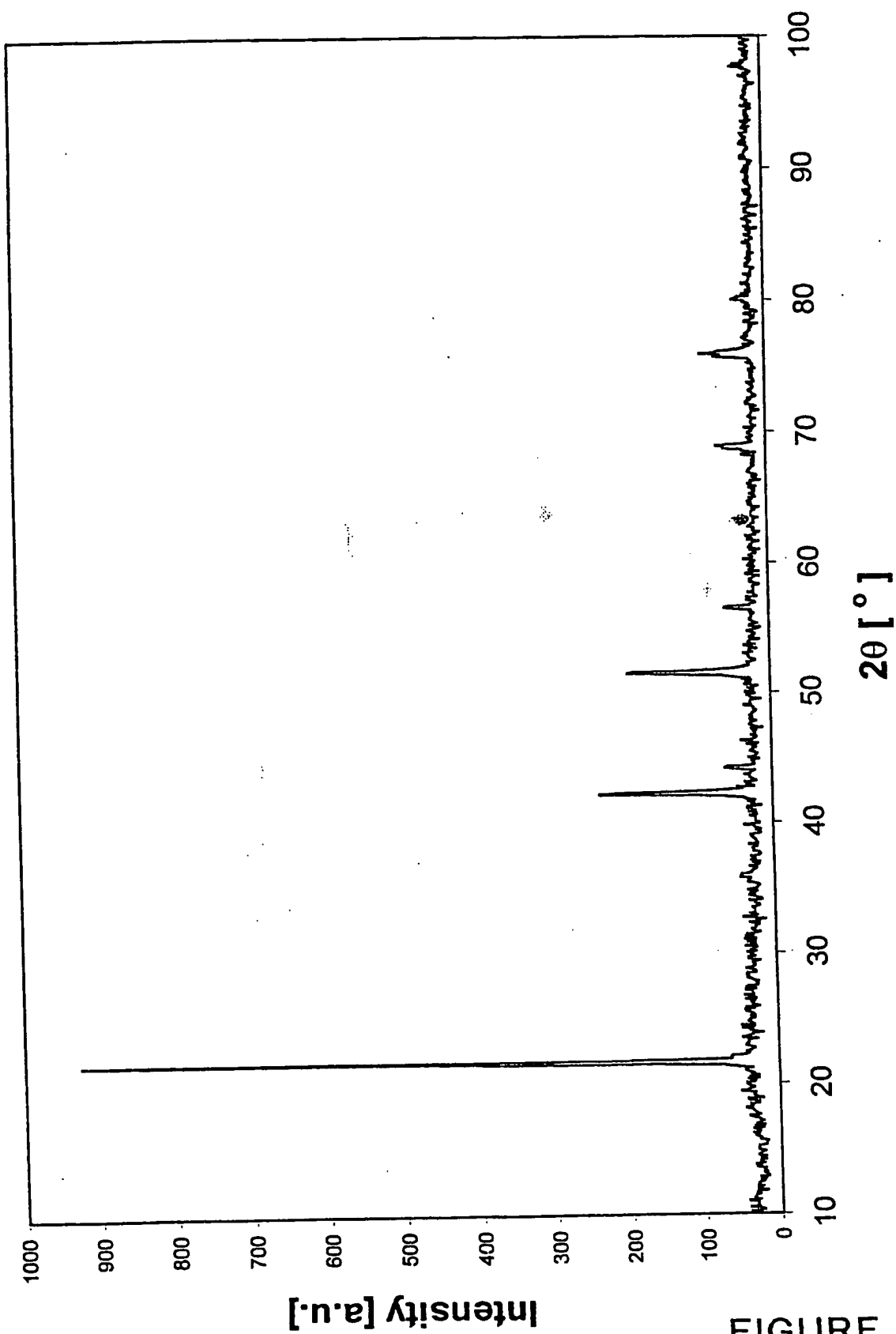
FIGURE 10A

FIGURE 10B
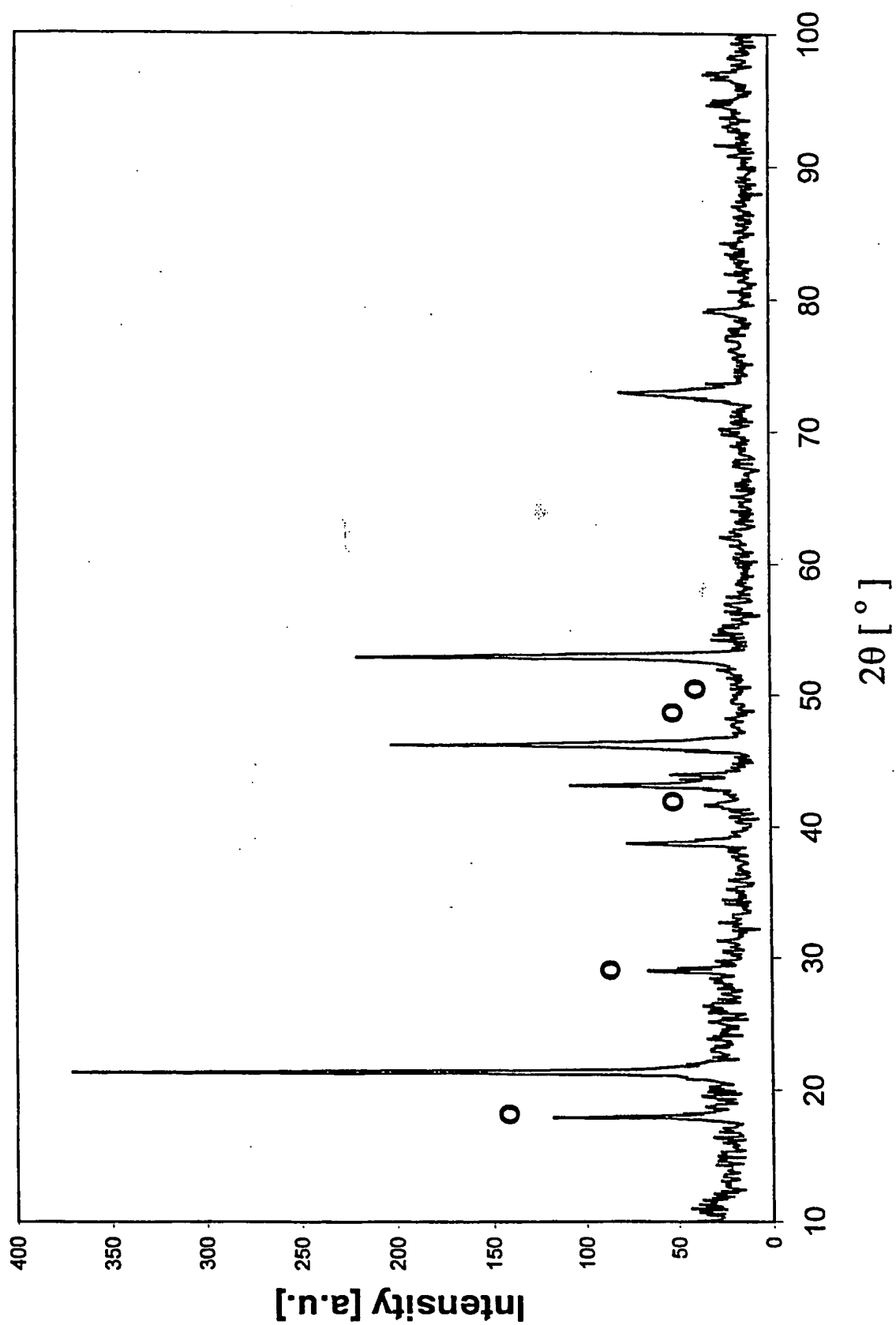
FIGURE 11A
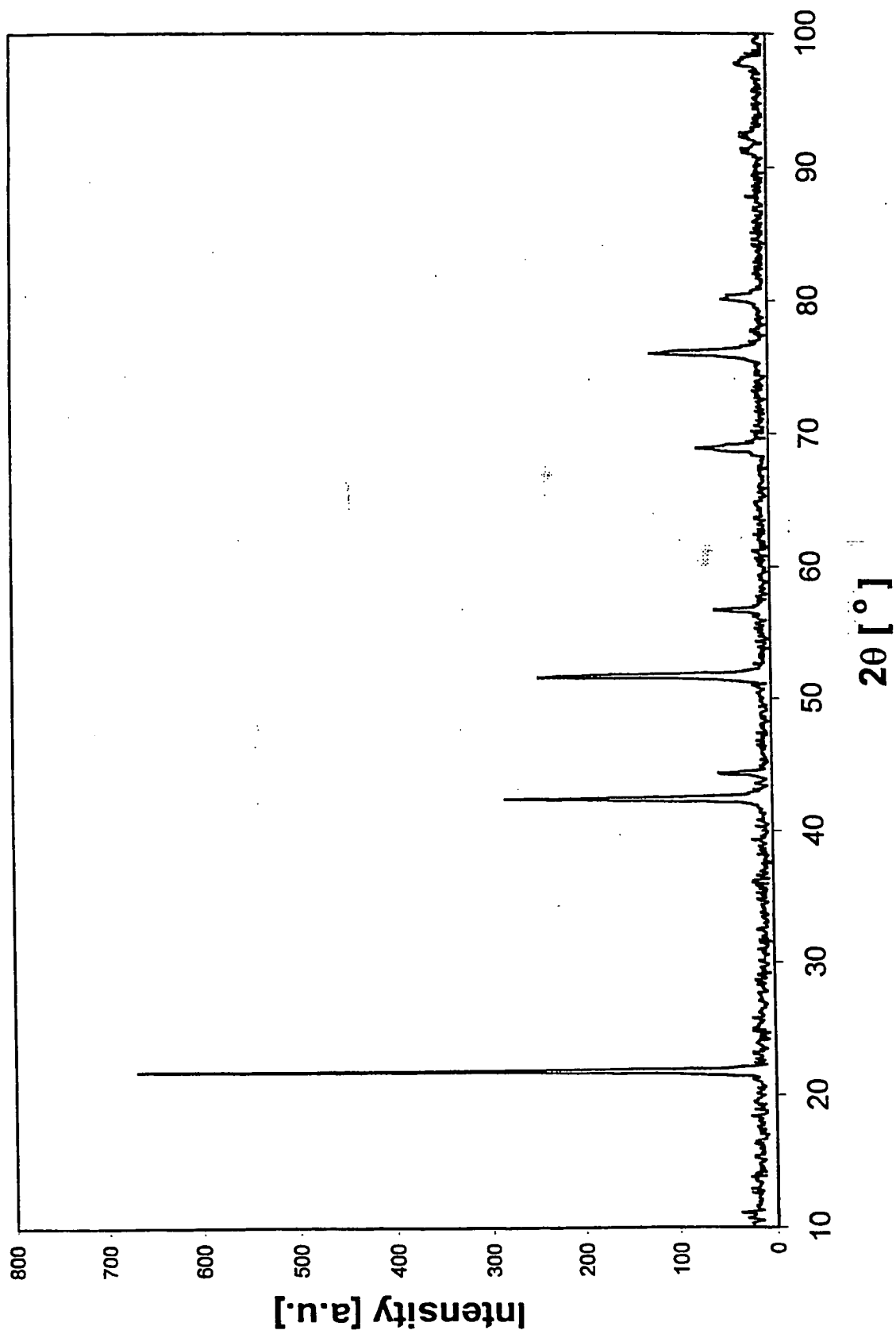
FIGURE 11B

FIGURE 12A
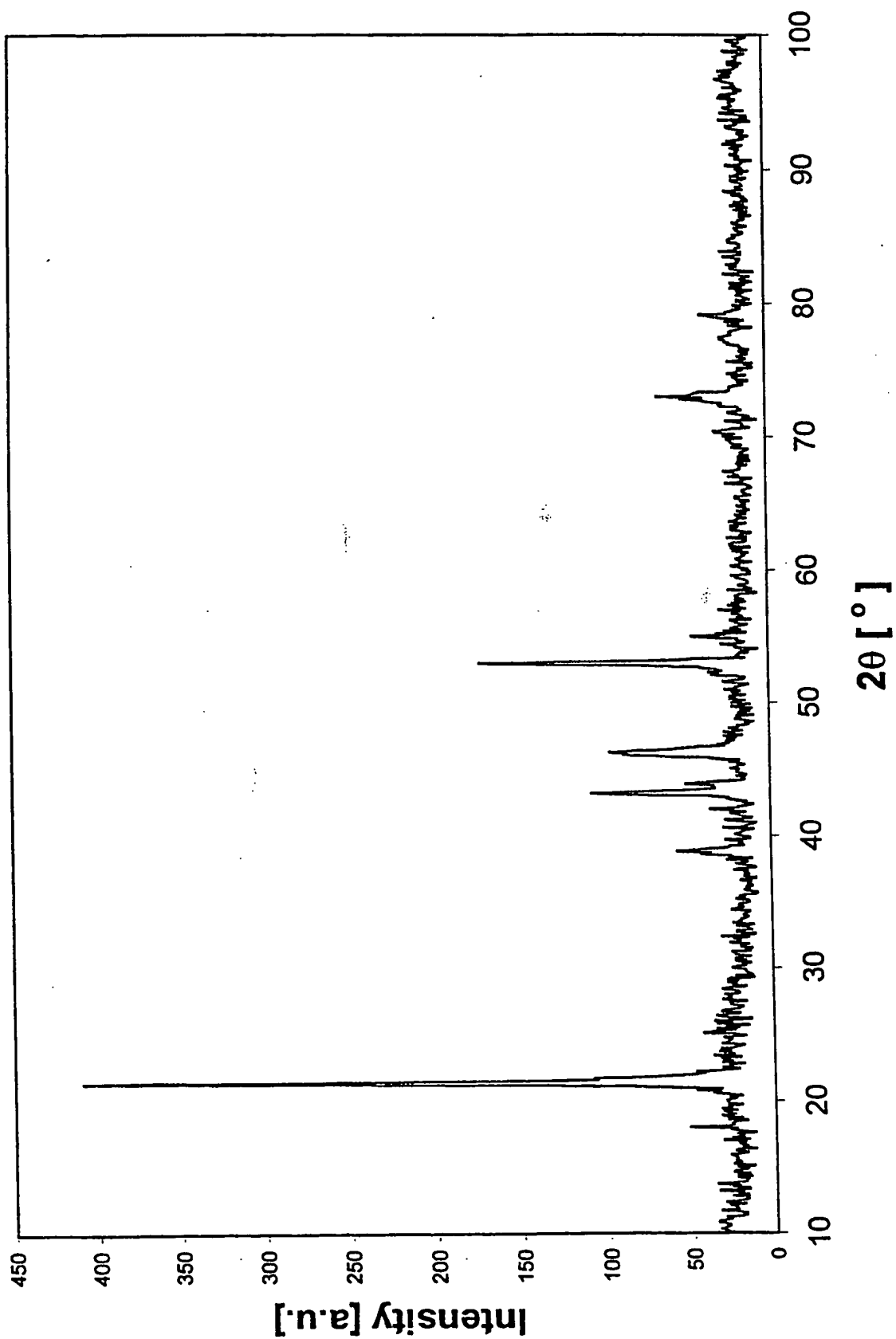
FIGURE 12B
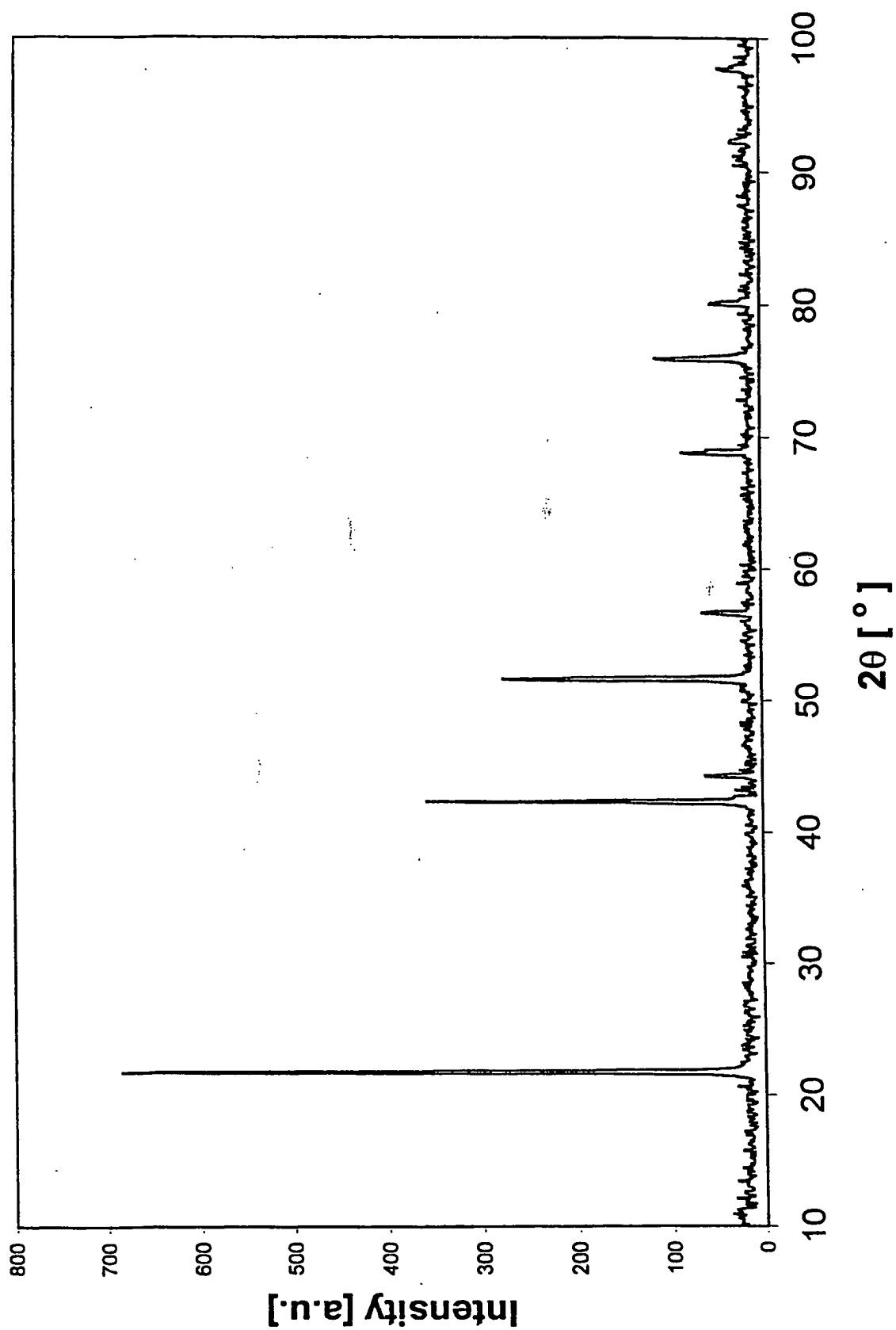
FIGURE 13A

FIGURE 13B
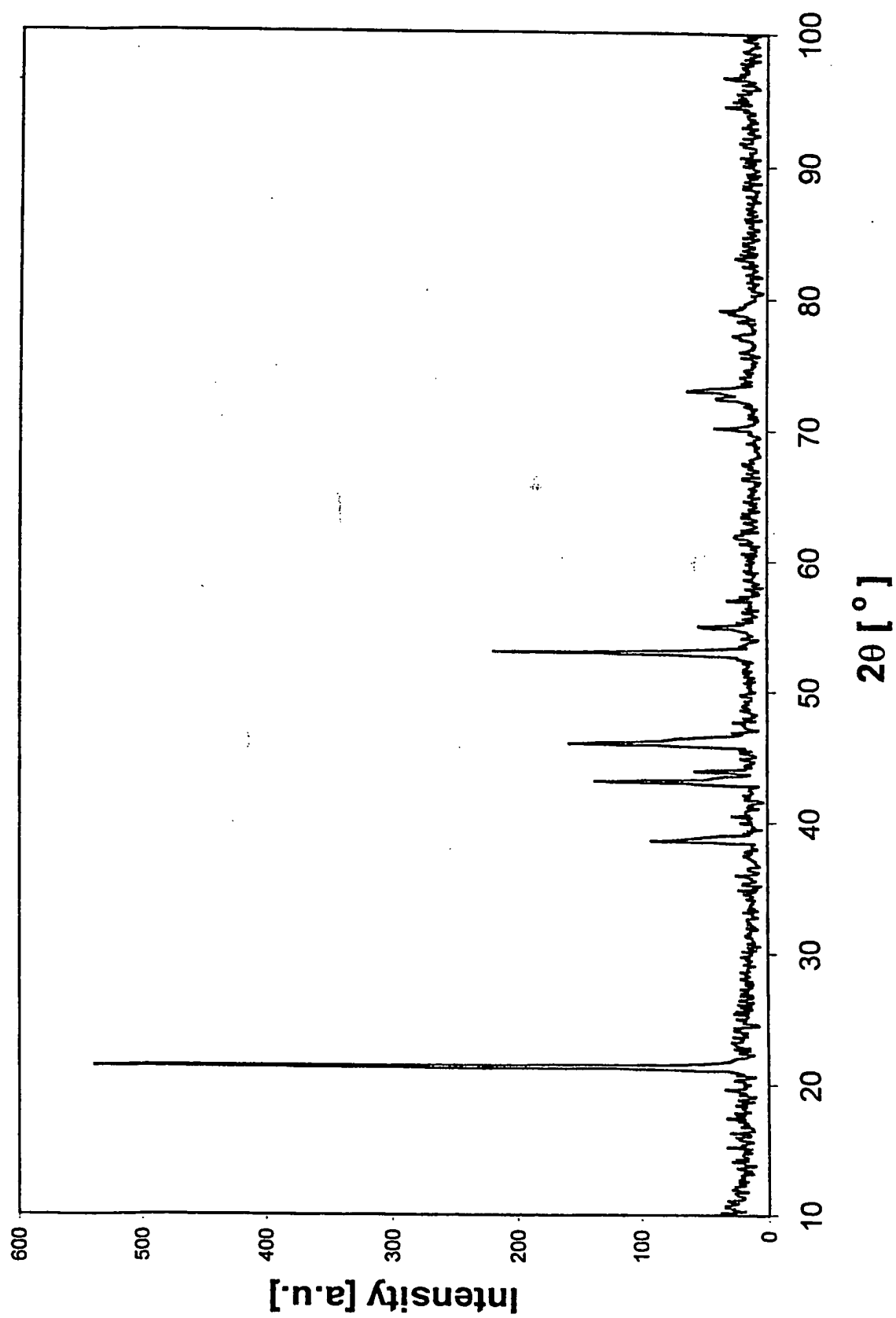
FIGURE 13C

FIGURE 13D

	International application No.
	PCT/NZ 99/00175

A.	**CLASSIFICATION OF SUBJECT MATTER**

Int Cl^6:   C01D 15/02; C01G 45/02; H01M 4/50, 4/58

According to International Patent Classification (IPC) or to both national classification and IPC

B.	**FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
C01D 15/02, 15/00; C01G 45/02, 45/00; H01M 4/50, 4/48, 4/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT, CASM, JAPIO

C.	**DOCUMENTS CONSIDERED TO BE RELEVANT**	

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 782206 A (Japan Storage Battery Co) 2 July 1997 See whole document	1, 4-5, 54-56
X	WO 98/02928 A (SAFT) 22 January 1998. See abstract, claims 1&2	1, 4-7, 54-56
X	Derwent Abstract Accession No. 98-353168, Class L03, JP 10134812 A (Matsushita) 22 May 1998 See abstract	1, 6-7, 54-56

[X] Further documents are listed in the continuation of Box C	[X] See patent family annex

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 January 2000	**0 1 FEB 2000**

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	**JAMES DZIEDZIC** Telephone No.: (02) 6283 2495

INTERNATIONAL SEARCH REPORT

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No . 98-039244, Class L03, JP 09293508 A (Sony) 11 November 1997 See abstract	1, 4-7, 54-56
X	Derwent Abstract Accession No. 97-391042 Class X16, JP 09171824 A (Matsushita) 30 June 1997 See abstract	1,4, 54-56
X	Derwent Abstract Accession No. 97-070344, Class L03, JP 08315819 A (Yuasa) 29 November 1996 See abstract	1, 4-5, 54-56
X	Derwent Abstract Accession No. 96-214217 Class L03, JP 08078009 A (Yuasa) 22 March 1996 See abstract	1,4,6, 54-56
X	Derwent Abstract Accession No. 96-214215 Class L03, JP 08078007 A (Yuasa) 22 March 1996 See abstract	1,4,5, 54-56

INTERNATIONAL SEARCH REPORT
Information on patent family members

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP	782206	CN	1156910	JP	9237631	US	5718989
		US	5795558				
WO	98/02928	CA	2228671	EP	858677	FR	2751135
						END OF ANNEX	